REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978
APPLICATION FOR A PATENT AND
ACKNOWLEDGEMENT OF RECEIPT
(Section 30(1) Regulation 22)

FORM P.1
(to be lodged in duplicate)

THE GRANT OF A PATENT IS HEREBY REQUESTED BY THE UNDERMENTIONED APPLICANT
ON THE BASIS OF THE PRESENT APPLICATION FILED IN DUPLICATE.

A & A REF: 118904 AS/CST

PATENT APPLICATION NO.		
21	01	89/6852
71	FULL NAMES(S) OF APPLICANT(S)	

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54	TITLE OF INVENTION

CROSS-LINKING OF POLYMERIC MATERIALS

Only the items marked with an "X" in the blocks below are applicable.

[X] The Applicant claims priority as set out on the accompanying Form P.2

[ ] The application is for a patent of addition to patent application no. |21|01|

[ ] This application is a fresh application in terms of section 37 and based on Application No.
|21|01|

THIS APPLICATION IS ACCOMPANIED BY:

[X] A single copy of a provisional or two copies of a complete specification of . 22..pages.

[ ] Drawing of .. ... sheets.

[X] Publication particulars and abstract (Form P.8 in duplicate) (for complete only).

[ ] A copy of Figure......of the drawings (if any) for the abstract (for complete only).

[X] An assignment of invention.

[ ] Certified priority document(s) (State quantity):.........

[ ] Translation of the priority document(s).

[ ] An assignment of priority rights.

[X] A copy of Form P.2 and the specification of RSA Patent Application No. |21|01| 88/5702

[X] A Form P.2 in duplicate.

[X] A declaration and power of attorney on Form P.3.

[ ] Request for ante-dating on Form P.4.

[ ] Request for classification on Form P.9.

[ ] Request for delay of acceptance on Form P.4.

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DATED THIS 7TH DAY OF SEPTEMBER 1989

ADAMS & ADAMS
APPLICANTS PATENT ATTORNEYS

The duplicate will be returned to the applicant's
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REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

PUBLICATION PARTICULARS AND ABSTRACT
(Section 32(3)(a) - Regulations 22(1)(g) and 31)

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CLASSIFIED BY: ADAMS & ADAMS

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NOTE: The country must be indicated by its International Abbreviation -
see schedule 4 of the Regulations.

TITLE OF INVENTION

54

57 ABSTRACT (NOT MORE THAN 150 WORDS)

NUMBER OF SHEETS 23

The sheet(s) containing the abstract is/are attached.

If no classification is furnished, Form P.9 should accompany this form.
The figure of the drawing to which the abstract refers is attached.

ABSTRACT

The invention provides a method of producing a cured polymeric artifact from a polymeric thermoplastic starting material, the material of the artifact having reduced thermoplasticity relative to the starting material and exhibiting an enhanced degree of cross-linking relative to the starting material. The method includes subjecting a polymeric thermoplastic starting material, which is capable of being cross-linked by irradiation, to sufficient irradiation partially to cross-link the starting material to produce a thermoplastic partially cross-linked intermediate material. The thermoplasticity of the intermediate material is then reduced by heating it to raise its melting point. The invention also provides a method of making a partially cross-linked feedstocks and a master batch for use in making such artifacts.

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FORM P7

REPUBLIC OF SOUTH AFRICA
Patents Act, 1978

COMPLETE SPECIFICATION

(Section 30 (1) - Regulation 28)

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TITLE OF INVENTION

| 54 | CROSS-LINKING OF POLYMERIC MATERIALS |

THIS INVENTION relates to the production of artifacts comprising cured polymeric materials. More particularly the invention relates to a method of producing a cured polymeric artifact from a polymeric thermoplastic starting material, the

5 material of the artifact having reduced thermoplasticity relative to the starting material and exhibiting an enhanced degree of cross-linking relative to the starting material; to a method of making a partially cross-linked polymeric thermoplastic material suitable for use as a feedstock for the production of polymeric

10 artifacts and capable of being cured by heating to reduce its thermoplasticity; and to a method of making a master batch for use in the production of a cured polymeric artifact.

According to one aspect of the invention there is provided a method of producing a cured polymeric artifact from a polymeric

15 thermoplastic starting material, the material of the artifact having reduced thermoplasticity relative to the starting material and exhibiting an enhanced degree of cross-linking relative to the starting material, the method including the steps of:

subjecting a polymeric thermoplastic starting material,

20 which is capable of being cross-linked by irradiation, to sufficient irradiation partially to cross-link the starting material to produce a thermoplastic partially cross-linked intermediate material; and

reducing the thermoplasticity of the intermediate material

25 by heating it to raise its melting point.

By raising the melting point of the intermediate material by heating is meant that, after such heating and subsequent cooling to ambient temperature, a product material will be obtained which has reduced thermoplasticity relative to the

30 intermediate material in the sense that, when the product material is again heated, its melting point will be higher than the melting point of the intrmediate material.

The polymeric thermoplastic starting material may be based on any suitable polymeric thermoplastic base material, which may be a plastics, resinous or elastomeric [rubbery] material, and will typically contain a suitable proportion of a suitable cross-

5   linking agent. Examples of base materials include homopolymers, co-polymers and ter-polymers of plastics material and rubbers which are thermoplastic, and blends thereof, eg polyethylene, polyvinyl chloride, segmented copolymers of butadiene and isoprene with styrene, natural rubber and polyethylene-ethylene

10 propylene rubber blends. Accordingly, the starting material may comprise a mixture of a polymeric thermoplastic base material and a cross-linking agent, the base material being selected from the group consisting of:

polyethylene;

15 polyvinyl chloride;

segmented copolymers of butadiene and isoprene with styrene;

natural rubber;

blends of polyethylene, ethylene and propylene rubber; and

mixtures of the aforegoing,

20 the mixture being in the form of a continuous phase of the base material in which the cross-linking agent is a discontinuous phase dispersed in finely divided form.

The method may include the preliminary steps of compounding or formulating the starting material, by admixing with the

25 polymeric base material or base materials a suitable cross-linking agent. Usually the cross-linking agent will comprise at least two chemically reactive unsaturated bonds such as double bonds in its molecule, some of which unsaturated bonds react with the base material during the partial cross-linking under the

30 influence of the radiation to produce the intermediate material. Suitable cross-linking agents include multifunctional acrylates or methacrylates such as trimethylolpropane trimethacrylate [TRIM] and allyl derivatives such as triallyl cyanurate [TAC]; and the material may be compounded to contain 0,5-25% by mass of

35 cross-linking agent. Compounding the material may take place in the usual way, eg by mixing the constituents to a sufficient

degree of homogeneity in the molten state at a temperature of typically not greater than 165°C and usually somewhat lower, and allowing the mixture to cool and set. Accordingly, in a particular embodiment, the method may include the preliminary
5   step, before the irradiation, of compounding or formulating the starting material by admixing a cross-linking agent into a molten polymeric thermoplastic base material, the cross-linking agent comprising at least two unsaturated bonds in its molecule, which bonds are capable of reacting with the base material under the
10   influence of the irradiation to cross-link the base material, the starting material being allowed to set before the irradiation is carried out.

The partial cross-linking may be effected by subjecting said material to ionising radiation, and may be effected at ambient
15   temperature. Alpha, beta or gamma radiation may be employed, and can be produced by a suitable radioactive isotope such as cobalt 60 or a suitable electron beam accelerator which generates energetic electrons with an energy of eg 50 keV to 10 MeV. The absorbed radiation dose applied to said material during the
20   partial cross-linking may be of the order of 4-100 kGy, and conventional electron beam machines or irradiators such as gamma irradiators can be employed for this purpose. In particular, the irradiation to which the starting material is subjected may be carried out at ambient temperature with the starting material in
25   solid form by subjecting the starting material to sufficient radiation to apply an absorbed radiation dose to the starting material of 4-100 kGy.

The degree of cross-linking effected during the partial cross-linking by irradiation will be sufficient to provide an
30   intermediate material which is thermoplastic; and the cross-linking effected by the irradiation may be sufficient to bind 10-50% by mass of the material, as determined by Soxhlet solvent extraction. The eventual properties of the cured material in turn depend on the temperature to which the intermediate is
35   heated, the time spent at that temperature and the proportion of

cross-linking agent added, and heating will be for a period sufficient to provide the cured artifact product with the desired absence of or low level of thermoplasticity.

The method may include the step of subjecting the starting or intermediate material to a size reduction to render it particulate before the thermoplsticity of the intermediate material is reduced by heating.

In a particular embodiment of the invention, the method may include the steps of:

forming a master batch by admixing a cross-linking agent into a molten thermoplastic diluent polymeric material, the diluent polymeric material having a melting point at least 60°C less than that of the starting material;

subjecting the master batch to irradiation to cross-link the diluent polymeric material; and

admixing the master batch into a polymeric thermoplastic base material in molten form to form the starting material. The master batch may be allowed to cool and set before it is admixed into the base material; and the master batch may be subjected to a size reduction which renders it particulate before it is admixed to the base material.

As indicated above, in preferred embodiments of the invention, the cross-linking agent may be a member of the group consisting in multifunctional acrylates and methacrylates, multifunctional allyl derivatives and mixtures thereof; and the cross-linking by irradiation may be by ionizing radiation selected from alpha radiation, beta radiation, gamma radiation and mixtures thereof.

The heating may be to a temperature of 160-220°C for a period of 5-200 seconds, preferably to a temperature of 160-220°C for a period of 30-120 seconds. Generally the heating time will be inversely related to the temperature, a desired reduction in thermoplasticity being achieved more rapidly the higher the

temperature, bearing in mind constraints imposed by, on the one hand, the fact that too high a temperature can have adverse effects on the product material, and, on the other hand, too low a temperature can lead to unacceptably long cycle times. Generally routine experimentation will be employed to determine an acceptable or optimum temperature/time combination, bearing in mind practical and economic considerations.

The nature of the base polymer and the cross-linking agent and the proportion of cross-linking agent, the degree of partial cross-linking by radiation, the temperature of heating and the duration of such heating, etc, will be selected so that these parameters produce a product with the desired physical and chemical properties. As at least a rough guide, known base polymer/cross-linking agent formulations can be employed which, when fully cured by radiation, provide a product with desired physical and chemical properties.

The method may include, in addition to mixing the cross-linking agent into the base polymer, admixing one or more additives therein. Such additives include:

antioxidants [stabilizers] such as hindered phenol octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate;

ultra-violet radiation stabilizers such as poly-([6-[(1,1,3,3-tetramethyl butyl)-imino]-1,3,5-triazine-2,4-diyl][2-(2,2,6,6-tetramethyl piperidyl)-imino]-hexamethylene-[4-(2,2,6,6-tetramethyl piperidyl)-imino]);

plasticizers such as phthalic esters or epoxidized soya oil;

impact modifiers such as ethylene-vinyl acetate copolymer or nitrile rubber;

slipping agents such as oleamide;

fillers such as calcium carbonate;

reinforcers such as carbon black;

flame retardants such as antimony trioxide and organobromine;

coupling agents such as silanes;

fungicides such as phosphites;

anti-blocking agents such as amide waxes;

pigments such as rutile;

essences such as dimethyl phenyl carbonyl;

lubricants such as stearic acid or calcium stearate;

5   blowing agents such as azodicarbonamide; and/or

electronic conductors such as carbon black.

The additives used and the proportions thereof used will be similar to those employed for similar purposes in polymeric materials which are usually fully cross-linked and cured by 10 irradiation.

An important feature of the invention arises from the fact that polymeric materials of the type in question are frequently employed by the conversion thereof in a fluid or a least mouldable state at an elevated temperature, eg by extrusion, 15   injection moulding, blow moulding, casting or the like, into numerous different artifacts or articles of commerce such as pipes, bottle crates etc. During fabrication of such artifacts by conversion, a starting material, which is thermoplastic and is typically in powder, granule or chip form, is formulated or 20   bought by the manufacturer of the artifact or article, and is converted at an elevated temperature, after which the article or artifact is caused or allowed to set. The artifact may thus be formed from a batch of material which has been heated to render it flowable, the forming being by moulding, casting or extruding 25   after which the artifact is allowed to set, the heating to reduce the thermoplasticity of the intermediate material taking place no earlier than the forming.

Accordingly, the forming and the heating to reduce the thermoplasticity may take place simultaneously, the heating which 30   acts to render the batch flowable also acting to effect the reduction in thermoplasticity. In other words, the heating of the intermediate material in terms of the method of the present invention may be carried out during such forming or conversion, eg during blow-moulding, injection-moulding, extruding, casting, 35   etc of the intermediate. Thus, the temperatures employed for the

forming or conversion have been found to be suitable for, or can be selected to be suitable for, the heating step of the method of the present invention, and can be held during conversion for a period sufficient to effect the reduction in thermoplasticity. It follows that the composition of the starting material which is irradiated to provide the partial cross-linking, and the degree of cross-linking effected by radiation, are conveniently selected to provide an intermediate material which is suitable as a feedstock for a forming or conversion process of the type in question. In particular, the method of the present invention may be carried out to provide an intermediate material which is suitable for use as a feedstock in conventional forming or conversion machinery in conventional conversion processes.

It follows that, after or conveniently before the irradiation but after any compounding or formulation to provide the starting material from a cross-linking agent and polymeric thermoplastic base material, the material being processed in accordance with the method of the present invention may be subjected to the abovementioned size reduction, so as to produce the intermediate material in powder, granule or chip form, suitable as a feedstock for subsequent forming or conversion processes.

The invention also extends to a cured polymeric artifact whenever produced by the method described above.

According to another aspect of the invention there is provided a method of making a partially cross-linked polymeric thermoplastic material suitable for use as a feedstock for the production of polymeric artifacts and capable of having its thermoplasticity reduced by heating, the method including the step of subjecting a polymeric thermoplastic starting material, which is capable of being cross-linked by irradiation, to sufficient irradiation partially to cross-link the starting material.

The polymeric material which is irradiated may be formulated and irradiated as described above, and, after or conveniently before irradiation, may be converted into particulate material as described above, to produce an intermediate material which can be employed as a feedstock for a variety of conversion processes, which conversion may indeed take place after elapse of a considerable period and at a different location.

As mentioned above, the method of producing a cured polymeric artifact according to the present invention can involve the use of a master batch. This master batch can, naturally, be compounded or formulated in one location and then can be transported or stored for use in another location, during the forming or conversion of a polymeric thermoplastic base material into a polymeric artifact.

Accordingly, a further aspect of the invention provides a method of making a master batch for use in a method of producing a cured polymeric artifact from a polymeric thermoplastics starting material as described above, the method of making the master batch comprising the steps of:

admixing a cross-linking agent into a molten thermoplastic polymeric base material having a melting point of at most 180°C; and

thereafter subjecting the mixture to irradiation to cross-link the polymeric material.

As indicated above, the polymeric base material for the master batch may be selected from the group consisting of:

polyethylene;

polyvinyl chloride;

segmented copolymers of butadiene and isoprene with styrene;

natural rubber;

blends of polyethylene, ethylene and propylene rubber; and

mixtures of the aforegoing,

the mixture being in the form of a continuous phase of the polymeric base material in which the cross-linking agent is a discontinuous phase dispersed in finely divided form.

The mixture may be allowed to cool and set before it is irradiated; and the mixture may be allowed to cool and set before then being subjected to size reduction which renders it particulate. As indicated above, the cross-linking by irradiation may be by ionizing radiation selected from alpha radiation, beta radiation, gamma radiation and mixtures thereof, and is sufficient to apply an absorbed radiation dose to the polymeric material of 4 - 100 kGy; and the cross-linking by irradiation may be sufficient to bind 10 - 50 % by mass of the polymeric material. As described above, the cross-linking agent may comprise at least two unsaturated bonds in its molecule, being a member of the group consisting of multifunctional acrylates and methacrylates, multifunctional allyl derivatives, and mixtures thereof. More particularly, formulation or compounding of the master batch may be as described in more detail above with reference to the method of producing a cured polymeric artifact, and it should be noted that the polymeric base material used for the master batch will typically have a melting point substantially lower than that of the polymeric base material for the artifact into which it is eventually intended to be blended, the polymeric base material of the master batch typically having a melting point of less than 165°C, eg 150°C or less. The invention contemplates that the master batch material, after cooling and solidification, will be milled into powder, granules or chips for transport or storage before required for use when it can be mixed into the base material employed for the artifacts in molten form, for use for forming or conversion into an artifact at which stage the heating is provided to reduce the thermoplasticity. Naturally, after it is mixed into the bulk of the base material for the artifact, it can, without heating sufficiently to reduce its theremoplasticity, again be cooled and milled and kept for use later, but usually conversion and heating to raise the melting point will take place immediately after the

to raise the melting point will take place immediately after the

blending. The base material for the master batch will naturally also be chosen so that it is physically and chemically compatible with the base material used for the eventual artifact.

5   The invention accordingly extends also to a master batch whenever made according to the method described above.

       The invention will now be described, by way of non-limiting illustrative example, with reference to the following worked Examples.

10   EXAMPLE 1
       A base material comprising Alkathene type polyethylene of grade LM3060P obtained from AECI Chlor-Alkali and Plastics Limited, Johannesburg was compounded with 1,5% by mass of TAC by blending in molten form at
15   150°C to form a substantially homogeneous mixture, together with 3 parts by mass of antioxidant stabilizer for every 100 parts by mass of polyethylene. The stabilizer was a hindered phenolic antioxidant introduced by said supplier.

20   The blend was allowed to set, divided into chips and was subjected to an absorbed dose of 25 kGy gamma radiation in a commercial gamma irradiator to effect partial cross-linking.

       The chips obtained were found to be thermoplastic and
25   capable of having their thermoplasticitiy reduced by heating to 165°C for about 1 minute into a fully cured non-thermoplastic product material. The degree of partial cross-linking achieved by the irradiation was found by Soxhlet extraction to be about 15% by mass of
30   that in the heated product; and the chips after irradiation were found to be suitable as a feedstock

for conversion into articles of commerce by conversion processes operating at 165°C.

EXAMPLE 2

Example 1 was repeated except that Corvic type S6617 grade LBH polyvinyl chloride obtained from PVC Compounders [Proprietary] Limited, Benoni, Transvaal was used instead of the polyethylene as the base material. The cross-linking agent was TRIM and 10 parts by mass of said cross-linking agent for every 100 parts of polyvinyl chloride was used. The antioxidant stabilizer used was 4 parts by mass of a zinc-free barium/cadmium mixture for every 100 parts of polyvinyl chloride.

A 50 kGy absorbed dose was employed. Additional additives which were employed in the compounding of the material for cross-linking were:

Constituent	parts by mass/ 100 parts by mass of poly- vinyl chloride
di-iso-octyl-phthalate [plasticiser]	90
epoxidized soya oil [secondary plasticizer stabilizer/extender]	4
stearic acid [internal lubricant]	0,2
calcium stearate [external lubricant]	1
nitrile rubber [impact modifier]	25
carbon black [pigment]	0,5

A thermoplastic intermediate was again obtained. This intermediate had about 37% by mass cross-linking [by Soxhlet extraction] and was capable of having its thermoplasticity reduced by heating to 165°C for about 1 minute, to obtain a non-thermoplastic product. The intermediate was again suitable for use as a feedstock for conversion at 165°C to produce artifacts by suitable conversion processes.

The invention, particularly as described with reference to the Examples, provides in principle certain substantial potential advantages and advances in the art when compared with similar methods known to the Applicant, whereby similar

5   formulations compounded from thermoplastic polymeric base materials and cross-linking agents, together with similar additives, are cured exclusively by irradiation.

An important such advantage is that the present invention overcomes the problem of said prior methods that size

10   constraints are imposed on the artifact or article of commerce which can be made. In the prior process, the article eg a large extrusion such as an extruded large diameter pipe or a large moulding, such as a bottle crate, must be extruded or moulded before cross-linking by radiation, while the formulation which

15   has been compounded is still thermoplastic, bearing in mind that full curing by radiation renders the material non-thermoplastic. If the article produced by the conversion is too large for the irradiator or electron beam machine in question, cross-linking, with its attendant advantages of superior physical and chemical

20   properties for many applications, must be dispensed with. In other words, the size, physical dimensions and design [shape] of the article produced by the conversion are limited by the size and design of the irradiation facility [irradiator or electron beam machine], which effectively rules out irradiation of

25   certain artifacts by means of small irradiators or electron beam machines.

In contrast, the Applicant has found that a variety of base materials, when compounded with suitable proportions of suitable accelerators or cross-linking agents of the type generally used

30   for irradiation curing, are capable of initial partial cross-linking by irradiation, after which reduction in thermoplasticity can be taken further simply by heating. This is particularly surprising as the Applicant has found that none of the base materials which it has tested, after compounding

with cross-linking agents, is suitable for cross-linking, thereby to obtain reduced thermoplasticity, merely by heating. It appears that the initial partial cross-linking by irradiation can be regarded as unexpectedly providing a product whose
5 thermoplasticity can be reduced, and whose melting point can be raised, merely by heating.

Importantly, sufficient cross-linking can be achieved by irradiation to make possible a reduction in thermoplasticity by sufficient subsequent heating, without unacceptable loss of the
10 thermoplastic nature of the intermediate material so that, after irradiation, conventional conversion processes, which rely on the thermoplastic nature of their feedstock for utility, can be used on the intermediate material. Furthermore the temperatures at which such conventional conversion processes operate, and the
15 periods for which the feedstock is held at such temperatures, have been found to be suitable for the reduction of thermoplasticity, which reduction in thermoplasticity can easily be effected by routine operation, without substantial modification, if any, of such conversion processes or machines.

20 The intermediate of the present invention thus constitutes a potentially valuable commercial feedstock, as it can be used to make products by conversion without limitation caused by the irradiation facility as to size, physical dimensions, design or shape of the product. Large pipes can be extruded, eg up to
25 1000 mm diameter or more, and large mouldings of complex shape such as bottle crates, can be moulded by blow moulding or extrusion moulding. The size of the product is limited only by what the conversion process can make, and not by what the irradiator or electron beam machine can handle.

30 The Applicant thus contemplates compounding suitable materials for irradiation, converting them into chip or other suitable particulate form, and conveying them continuously in chip form, eg on a suitable conveyor at high production rates through an irradiator or electron beam machine which can be of

relatively small size. The partially cross-linked thermoplastic intermediate of the invention thus lends itself to efficient mass production using an irradiator or electron beam machine of any size; and can then be used or sold to users as a feedstock
5   which can be used on conversion machines and in conversion processes requiring little if any modification to handle it.

Particular applications of the invention are in the manufacture of pipes of a diameter too great to be handled by presently available irradiations or electron beam machines; and
10   the manufacture of articles such as bottle crates which are subject to theft by persons who render them into chips as feedstock for other conversion processes if they are of sufficiently thermoplastic material. When made by the present method, such crates or the like can be of a cross-linked
15   material which is sufficiently non-thermoplastic to be unsuitable as feedstock, and will not be stolen for this purpose.

CLAIMS

1.   A method of producing a cured polymeric artifact from a
polymeric thermoplastic starting material, the material of the
artifact having reduced thermoplasticity relative to the
5   starting material and exhibiting an enhanced degree of cross-
linking relative to the starting material, the method including
the steps of:
        subjecting a polymeric thermoplastic starting material,
which is capable of being cross-linked by irradiation, to
10 sufficient irradiation partially to cross-link the starting
material to produce a thermoplastic partially cross-linked
intermediate material; and
        reducing the thermoplasticity of the intermediate material
by heating it to raise its melting point.

15 2.   A method as claimed in claim 1, in which the starting
material comprises a mixture of a polymeric thermoplastic base
material and a cross-linking agent, the base material being
selected from the group consisting of:
polyethylene;
20 polyvinyl chloride;
segmented copolymers of butadiene and isoprene with styrene;
natural rubber;
blends of polyethylene, ethylene and propylene rubber; and
mixtures of the aforegoing,
25 the mixture being in the form of a continuous phase of the base
material in which the cross-linking agent is a discontinuous
phase dispersed in finely divided form.

3.   A method as claimed in claim 1 or claim 2, which includes
the preliminary step, before the irradiation, of compounding or
30 formulating the starting material by admixing a cross-linking
agent into a molten polymeric thermoplastic base material, the

cross-linking agent comprising at least two unsaturated bonds in its molecule, which bonds are capable of reacting with the base material under the influence of the irradiation to cross-link the base material, the starting material being allowed to set before the irradiation is carried out.

4.   A method as claimed in any one of the preceding claims, in which the irradiation to which the starting material is subjected is carried out at ambient temperature with the starting material in solid form by subjecting the starting material to sufficient radiation to apply an absorbed radiation dose to the starting material of 4-100 kGy.

5.   A method as claimed in any one of the preceding claims, in which the cross-linking effected by the irradiation is sufficient to bind 10-50% by mass of the starting material, as determined by Soxhlet solvent extraction.

6.   A method as claimed in any one of the preceding claims, which includes the step of subjecting the starting or intermediate material to a size reduction to render it particulate before the thermoplasticity of the intermediate material is reduced by heating.

7.   A method as claimed in claim 1 or claim 2 , which includes the steps of:
    forming a master batch by admixing a cross-linking agent into a molten thermoplastic diluent polymeric material, the diluent polymeric material having a melting point at least 60°C less than that of the starting material;
    subjecting the master batch to irradiation to cross-link the diluent polymeric material; and
    admixing the master batch into a polymeric thermoplastic base material in molten form to form the starting material.

8. A method as claimed in claim 7, in which the master batch is allowed to cool and set before it is admixed into the base material.

9. A method as claimed in claim 8, in which the master batch is subjected to a size reduction which renders it particulate before it is admixed into the base material.

10. A method as claimed in any one of the preceding claims, in which the cross-linking agent is a member of the group consisting of multifunctional acrylates and methacrylates, multifunctional allyl derivatives and mixtures thereof.

11. A method as claimed in any one of the preceding claims, in which the cross-linking by irradiation is by ionizing radiation selected from alpha-radiation, beta radiation, gamma radiation and mixtures thereof.

12. A method as claimed in any one of the preceding claims, in which the heating is to a temperature of 160 - 220°C for a period of 5 - 200 seconds.

13. A method as claimed in any one of the preceding claims, in which the artifact is formed from a batch of material which has been heated to render it flowable, the forming being by moulding, casting or extruding after which the artifact is allowed to set, the heating to reduce the thermoplasticity of the intermediate material taking place no earlier than the forming.

14. A method as claimed in claim 12, in which the forming and heating to reduce the thermoplasticity take place simultaneously, the heating which acts to render the batch flowable also acting to effect the reduction in theremoplasticity.

15. A method of producing a cured polymeric artifact from a polymeric thermoplastic starting material, the material of the artifact having reduced thermoplasticity relative to the starting material and exhibiting an enhanced degree of cross-
5   linking relative to the starting material, the method being substantially as described herein.

16. A cured polymeric artifact whenever produced by the method of any one of the preceding claims.

17. A method of making a partially cross-linked polymeric
10   thermoplastic material suitable for use as a feedstock for the production of polymeric artifacts and capable of having its thermoplasticity reduced by heating, the method including the step of subjecting a polymeric thermoplastic starting material, which is capable of being cross-linked by irradiation, to
15   sufficient irradiation partially to cross-link the starting material.

18. A method as claimed in claim 17, in which the starting material comprises a mixture of a polymeric thermoplastic base material and a cross-linking agent, the base material being
20   selected from the group consisting of:
polyethylene;
polyvinyl chloride;
segmented copolymers of butadiene and isoprene with styrene;
natural rubber;
25   blends of polyethylene, ethylene and propylene rubber; and
mixtures of the aforegoing,
the mixture being in the form of a continuous phase of the base material in which the cross-linking agent is a discontinuous phase dispersed in finely divided form.

30   19. A method as claimed in claim 17 or 18, which includes the preliminary step, before the irradiation, of compounding or formulating the starting matertial by dissolving a cross-linking agent in a molten polymeric thermoplastic base material, the

cross-linking agent comprising at least two unsaturated bonds in its molecule, which bonds are capable of reacting with the base material under the influence of the irradiation to cross-link the base material, the starting material being allowed to set
5   before the irradiation is carried out.

20.   A method as claimed in claim 18 or claim 19, in which the cross-linking agent is a member of the group consisting of multifunctional acrylates and methacrylates, multifunctional alkyl derivatives and mixtures thereof.

10   21.   A method as claimed in any one of claims 17 to 20 inclusive, in which the irradiation to which the starting material is subjected is carried out at ambient temperature with the starting material in solid form by subjecting the starting material to sufficient ionizing radiation selected from the
15   group consisting of alpha radiation, beta radiation, gamma radiation and mixtures thereof, to apply an absorbed radiation dose to the starting material of 4-100 kGy.

22.   A method as claimed in any one of claims 17 to 21 inclusive, in which the cross-linking effected by the
20   irradiation is sufficient to bind 10-50% by mass of the starting material, as determined by Soxhlet solvent extraction.

23.   A method as claimed in any one of claims 17 to 22 inclusive, which includes the step of subjecting the starting material to a size reduction to render it particulate.

25   24.   A method of making a partially cross-linked polymeric thermoplastic material suitable for use as a feedstock for the production of polymeric artifacts and capable of having its thermoplasticity reduced by heating, substantially as described herein.

30   25.   A partially cross-linked polymeric thermoplastic material suitable for having its thermoplasticitiy reduced by heating,

whenever made according to the method of any one of claims 17 to 24 inclusive.

26. A method of making a master batch for use in a method as claimed in claim 7, the method comprising the steps of:

   admixing a cross-linking agent into a molten thermoplastic polymeric base material having a melting point of at most 180°C; and

   thereafter subjecting the mixture to irradiation to cross-link the polymeric material.

27. A method as claimed in claim 26, in which the polymeric base material is selected from the group consisting of:
polyethylene;
polyvinyl chloride;
segmented copolymers of butadiene and isoprene with styrene;
natural rubber;
blends of polyethylene, ethylene and propylene rubber; and
mixtures of the aforegoing,
the mixture being in the form of a continuous phase of the polymeric base material in which the cross-linking agent is a discontinuous phase dispersed in finely divided form.

28. A method as claimed in claim 26 in which the mixture is allowed to cool and set before it is irradiated.

29. A method as claimed in any one of claims 26 to 28 inclusive, in which the mixture is allowed to cool and set and is then subjected to size reduction which renders it particulate.

30. A method as claimed in any one of claims 26 to 29 inclusive, in which the cross-linking by irradiation is by ionizing radiation selected from alpha radiation, beta radiation, gamma radiation and mixtures thereof, and is sufficient to apply an absorbed radiation dose to the polymeric material of 4 -100 kGy.
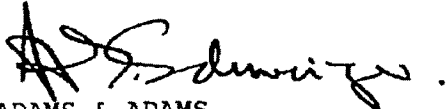
31. A method as claimed in any one of claims 26 to 30 inclusive, in which the cross-linking by irradiation is sufficient to bind 10 - 50% by mass of the polymeric material.

32. A method as claimed in any one of claims 26 to 31 inclusive, in which the cross-linking agent comprises at least two unsaturated bonds in its molecule, and is a member of the group consisting of multifunctional acrylates and methacrylates, multifunctional alkyl derivatives, and mixtures thereof.

33. A method of making a master batch for use in a method as claimed in claim 7, substantially as described herein.

34. A master batch for use in a method as claimed in claim 7, whenever made according to the method of any one of claims 26 to 33 inclusive.

DATED THIS 7TH DAY OF SEPTEMBER 1989

ADAMS & ADAMS
APPLICANTS PATENT ATTORNEYS

(12) **EUROPEAN PATENT SPECIFICATION**

(54) THE PREPARATION OF ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE MORPHOLOGIES OF TOTALLY FUSED PARTICLES WITH SUPERIOR MECHANICAL PERFORMANCE.

EP 0 177 552 B1

Description

Cross Reference to Related Application

Co-pending patent application No. 578,171, filed February 8, 1984, relates to a solid state deformation process for achieving the production of high modulus and high-strength polymers in simple and complex shapes at rapid output rates and moderate processing conditions.

Field of Invention

This invention relates to a novel type of ultra-high-molecular-weight polyethylene with superior modulus and elastic response performance and the method of making it.

Ultra-high molecular weight polyethylene has been defined by ASTM D 4020-81 as those linear polyethylenes which have a relative viscosity of 2.3 or greater at a solution concentration of 0.05% at 135°C. in decahydronaphthalene. The nominal weight-average molecular weight is several million, usually from three to six million.

Background of the Invention

Various polymer systems have been investigated for such uses as the preparation of artificial prostheses for biomedical, particularly orthopedic applications. The objective has usually been to duplicate the mechanical properties of the natural counterparts and to meet the requirements of tissue biocompatibility. For example, the preparation of artificial tendons has been pursued basically by the construction of composite structures of fiber-reinforced elastomers, such as poly(ethylene terephthalate) in silicone rubber. Silk and metal fibers have also been used as components in such prostheses. The fiber-reinforced elastomers, such as poly(ethylene terephthalate) in silicone rubber. Silk and metal fibers have also been used as components in such prostheses. The fabrication of tapes and fiber meshes using conventional polymers, e.g., nylon, dacron, and polyethylene has also been explored. In the latter case, however, nylon has been found to degrade in vivo; dacrons have been found to fail in tissue ingrowth tests; and conventional polyethylene when strained in the working range of human tendons (3% strain), has been unsatisfactory both in its elastic recovery (80-90%) and in the time needed for complete recovery (5 min.) --two important factors in the design of artificial tendons.

Ligament fabrication has been pursued by the design of artificial preparations utilizing ultra-high-molecular-weight polyethylene. Ultra-high molecular weight polyethylene, in contrast to the conven-

tional high-density polyethylenes having average molecular weight up to about 400,000, has an extremely high molecular weight--typically 2 to 6 million--and is intractable. The polymer is supplied as fine powder and is processed into various profiles using compression molding and ram extrusion processes. However, studies made heretofore have suggested that the ultra-high molecular weight polyethylene structures made by such processes do not possess adequate yield, creep, and fatigue properties to meet the requirements of biomedical applications, apparently because of poor interparticle fusion of the powder particles in the raw material during its processing. More recently, new processing systems, including ultra-high speed mixing systems and radio-frequency heating, have been used in injection molding practices to produce ultra-high molecular weight products. However, the products of such processes are obtained also in a temperature range (360-380 °F. 182 - 193°C.) in which it has been found that complete fusion of the powder particles does not occur. Furthermore, radio-frequency heating, an effective process for heating polymers such as nylons, PVC, and PVF$_2$ that have polar molecules to respond to radio-frequency energy is impractical for non-polar polymers such as polyethylene. Radio-frequency heating of such polymers can occur by incorporating in the polymer agents such as Frequon (a trademark of the Phillips Chemical Co.) which are sensitive to radio frequency. However, the use of additives in the polymer, which is known to be biocompatible, may have adverse effects in meeting the requirements of tissue biocompatibility in biomedical applications.

J. Appl. Polym. Sci, vol 28, (1983) pages 1837-45 refers to oriented ultra-high molecular weight polyethylene films prepared under compression and rotation. The melting temperatures discussed are at least 335°C. US-A-42 46 390 discloses ultra-high molecular weight polyethylene powders being heated at a temperature in the range of the crystalline melting point (at least about 140°C) to about 275°C from about 1 to about 30 minutes, typically a few minutes at 250°C and more than 30 minutes at 140°C.

Summary of the Invention

This invention protection for which is sought in the claims 1 to 23, provides the complete fusion of powder particles of ultra-high molecular weight polyethylene in an hitherto unexplored temperature range, resulting in a homogeneously melt crystallized morphology with no grain memory of the powder particles and the preparation of an anisotropic morphology with significantly enhanced modulus and superior elastic response perfor-

mance by solid state deformation techniques.

The present invention provides a homogeneously melt-crystallized morphology of ultra-high molecular polyethylene obtained by complete fusion of the powder particles of the raw material in a temperature range in which the powder particles fuse completely and have no memory of their granular structure prior to melting and during the inadequate melting which is practiced in currently used processes. The mechanical performance of such homogeneous melt crystallized morphologies of ultra-high molecular weight polyethylene are superior to the properties of commercially available products of ultra-high molecular weight polyethylene.

This invention provides also the preparation of an anisotropic morphology of ultra-high molecular weight polyethylene with significantly enhanced modulus and superior elastic response performance by the solid state deformation techniques of drawing and extrusion through an extrusion rolling die. This performance has been demonstrated both in laboratory testing and in vivo functional loads for biomedical applications.

According to the present invention, the preparation of the anisotropic morphology of ultra-high molecular-weight polyethylene comprises the steps of (1) preparing initially a uniform semicrystalline morphology by compression-molding an ultra-high molecular-weight polyethylene melt in a temperature range in which the melt has no memory of the granular nature of the original powder, and (2) solid-state deforming the so-produced uniformly melt-crystallized morphology by conventional drawing or by extruding it through an extrusion rolling die at a temperature preferably near but below its crystalline melting point and at a deformation ratio of 5-8. The deformation ratio is determined by the displacement of printed markers or fiducial marks on the surface of the drawn or extruded specimen or the cross-sectional areas of the samples before and after drawing or extrusion.

Brief Description of the Drawing

Fig. 1 is a graph showing the stress-elongation behavior at ambient temperature of two compression-molded specimens of ultra-high molecular weight polyethylene, one molded at 180°C and the other according to the present invention, at 320°C.

Fig. 2 is a similar graph contrasting the stress-strain behavior of three specimens of five-times-drawn ultra-high molecular weight polyethylene obtained by solid-state deforming of compression molded specimens at 180°C, and 210°C., and, according to the present invention, at 320°C.

Fig. 3 is a similar drawing, showing the stress-strain behavior under cyclic load tests at ambient temperatures of five-times-drawn ultra-high molecular weight polyethylene morphologies obtained by solid-state deformation of a compression-molded specimen at 180°C and, according to the present invention, at 320°C.

Fig. 4 is a diagrammatic cross-sectional view of a flexor tendon and related parts, employing the principles of this invention, indicating the tendon-bone and the muscle-tendon functions and the body of the tendon which was truncated to insert and suture the artificial tendon of ultra-high molecular weight polyethylene of this invention.

Description of Some Preferred Embodiments of the Invention

An ultra-high-molecular-weight polyethylene melt, in which the powder particles fuse completely and lose memory of their granular structure in the original powder stock, is achieved by heating the powder stock or partially fused, melt-crystallized morphology having granular memory -- in the absence of oxygen to avoid degradation, e.g., under nitrogen -- in a temperature range above 220°C. and below 340°C. the latter being the temperature at which excessive decomposition occurs under nitrogen. Isobaric heating at 320°C. under a compression load of 1500-2000 lbs. for 10 minutes followed by heating at 150°C. under a load of 12000-14000 lbs. for an additional 10 minutes and cooling to ambient under the same compression conditions results in a uniform or homogeneous melt-crystallized morphology with no grain memory. The resultant ultra-high molecular weight polyethylene morphology has superior mechanical performance in comparison to currently available products which are fabricated typically in the temperature range of 180-210°C and under similar pressure conditions.

Prior literature dictates that under these temperature and pressure conditions the powder particles should fuse completely. (The equilibrium melting temperature of ideal crystals of polyethylene is 141.4°C.) However, in the case of ultra-high molecular weight polyethylene such processing conditions result in a partial fusion as manifested from the grain memory of the original powder particles and the diminished mechanical properties. Complete fusion of the powder particles of ultra-high molecular weight polyethylene and consequently a uniform melt-crystallized morphology occurs by heating above 220°C. and results in superior mechanical properties in comparison to the properties exhibited by the prepared morphologies below 220°C., i.e., 180 - 210°C. Alternatively, a partially fused, melt-crystallized morphology with granular memory, typically obtained at tempera-

tures below 220°C., can be heated above 220°C. to obtain the complete fusion of this invention.

The partial fusion of the powder particles below 220°C. arises from the high melt viscosity (in the temperature range 145 - 210°C.) which hinders the formation of a molecular network between powder particles and to the high degree of physical entanglements which hinder chain mobility during the compression molding process; effective chain interpenetration between powder particles can occur upon heating the raw powder stock or a partially fused melt-crystallized stock with granular memory above 220°C. where the melt viscosity is significantly lower.

As shown in Fig. 1, the presence of a molecular network between powder particles in the compression molded specimen at 320°C. results in a significantly higher slope of stress to extension and strength to break (150 MPa), in comparison to a specimen molded at 180°C. which is comprised of partially fused powder particles and which fractured at 35-40 MPa.

Solid-state deformation of such homogeneously melt-crystallized morphologies previously prepared by compression molding at 320°C. take place by drawing or extrusion through an extrusion rolling die at 130°C and a deformation ratio 5-8 and result in anisotropic morphologies with superior mechanical properties in comparison to the five-times-drawn morphologies obtained by solid-state deformation of compression-molded at 180-200°C. For example, as shown in Fig. 2, the slope of stress to elongation of an anisotropic morphology of a five-times-drawn ultra-high molecular weight polyethylene sample prepared by compression molding at 320°C., is considerably higher than the slope of a five-times-drawn sample from a compression molded specimen at 210°C., and significantly higher than the slope of a five-times-drawn sample from a compression molded specimen at 180°C., evidently reflecting the higher degree of interparticle chain penetration which occurs by compression molding at higher temperatures.

The overall increase in the slope of load-to-elongation observed in Fig. 2, in comparison to the undrawn morphologies in Fig. 1, is associated with the chain extension and orientation of the five-times-drawn morphologies. The five-times-drawn morphologies from specimens compression molded at 320°C. have a Young modulus of 5-6 GPa,and in cyclic load tests under 40-45 MPa for testing up to 1 hour they deform practically elastically (see Fig. 3). On the contrary, as also shown in Fig. 3, the five-times-drawn morphologies from specimens compression molded at 180°C have a low Young modulus (0.7-0.8 GPa) and in cyclic load tests under the same conditions undergo a maximum residual elongation greater than 3%.

Tests In vivo indicate that artificial tendons made by this process can be sutured to the natural tendon segments readily and without fibrillation. It is significant that the ultra-high-molecular-weight polyethylene anisotropic morphologies in this invention do not exhibit a tendency to fibrillation, for this is in contrast to the fibrillation observed with conventional-molecular-weight (60,000 to 400,000) polyethylene analogues. Anisotropic products are strong only in the drawn direction in which the molecular chains are oriented and connected by covalent bonds but are extremely weak in their lateral direction because the chains are connected by weak Van der Waals forces, and consequently when a load is applied perpendicularly to the direction of chain orientation they tend to fibrillate along the chain direction. Although cross-linking by radiation or chemical additives have been used to alleviate the occurrence of fibrillation, the resistance to fibrillation of the ultra-high molecular weight polyethylene anisotropic morphology in this invention is due to the excessive amount of physical entanglement in the so-prepared initially homogeneous melt crystallized morphology.

Artificial tendons made according to the present invention exhibit very satisfactory anastomosis after an observation period of six weeks, and they replicate the properties of the natural tendons. For example, they have been found to replicate the properties of the tendon (Flexor Hollucis longus) of a dog weighing approximately 70 pounds, as demonstrated by the complete mobility of the dog during the six-week testing period. A lateral view of a flexor tendon indicating the tendon-bone and the musculo-tendon junctions and the body of the tendon which was truncated to insert and suture the artificial tendon of ultra-high molecular weight polyethylene is shown in Fig. 4.

The present invention also includes within its scope the use of the isotropic (the initially homogeneous melt-crystallized morphology, prepared from either a raw powder stock or a partially fused melt-crystallized stock with granular memory, prior to drawing or extrusion) and anisotropic ultra-high-molecular-weight polyethylene morphologies in other biomedical applications, e.g., ligament prostheses in which a high elastic recovery and a small percent strain under high load requirements are necessary. Furthermore, the homogeneity of the morphologies in this invention versus the partially fused morphologies used to date, is important in eliminating the fatigue failure observed with orthopedic prostheses which are fabricated from partially fused morphologies and also in the fabrication of orthopedic prostheses with abrasion resistance uses such as joints and intervertebral disks.

Other applications on which the homogeneity of the morphologies in this invention is important, is

in the fabrication of industrial parts with abrasion resistance uses such as bearings, sprockets, gaskets, ball valve seats, conveyor belt parts and other industrial parts currently made from metal.

To those skilled in the art to which this invention relates, many changes in construction and widely differing embodiments and applications of the invention will suggest themselves without departing from the spirit and scope of the invention. The disclosures and the descriptions herein are purely illustrative and are not intended to be in any sense limiting.

Claims

1.   A method for making an ultra-high-molecular-weight polyethylene (UHMW PE) having an isotropic semi-crystalline morphology comprising:

heating an original powder stock or a partially fused melt-crystallized stock of UHMW PE as defined by ASTM D 4020-81 having granular memory to a temperature of 220-320° C in the absence of oxygen to fuse the stock completely to form a homogeneous melt which loses memory of its former granular structure, and

cooling the resultant melt to ambient temperatures under compression to provide a UHMW PE having a homogeneous isotropic semi-crystalline morphology which has no memory of the granular nature of the original stock.

2.   The method of claim 1 wherein the heating step comprises heating at 320° C for about 10 minutes.

3.   A method for making an ultra-high-molecular-weight polyethylene (UHMW PE) having an isotropic homogeneous semicrystalline morphology comprising:

heating an original powder stock or a partially fused melt-crystallized stock of UHMW PE as defined by ASTM D 4020-81 having granular memory, at a temperature of 320° C in the absence of oxygen at a pressure of about 20-50 MPa for about ten minutes, then at about 150° C placing the material under a pressure of about 70-280 MPa for another ten minutes to provide a melt in which the stock fuses completely and loses memory of its former granular structure, and

cooling the resultant material to ambient temperature under a pressure of about 20 MPa to give a UHMW PE having a semicrystalline morphology which has no memory of the granular nature of the original stock.

4.   A method for making an ultra-high-molecular-weight polyethylene (UHMW PE) having an anisotropic morphology comprising:

heating an original powder stock or a partially fused melt-crystallized stock of UHMW PE as defined by ASTM D 4020-81 having granular memory to a temperature between 220 and 320° C in the absence of oxygen to fuse the stock completely and lose memory of its original granular structure,

cooling the resultant material to ambient temperatures under compression to provide a UHMW PE having an initial homogeneous isotropic semicrystalline morphology which has no memory of the granular nature of the original stock, and

solid-state deforming that semicrystalline UHMW PE at a temperature near but below its crystalline melting point at a deformation ratio of about 5 to 8.

5.   The method of claim 4 wherein the temperature of deformation is about 130° C.

6.   The method of claim 4 wherein the heating is accompanied by a compression pressure of about 20-50 MPa.

7.   The method of claim 6 wherein the heating step also includes heat at 150° C under a pressure of about 70-280 MPa.

8.   The method of claim 4 wherein the deforming step includes drawing at least five times.

9.   A method for making an ultra-high-molecular-weight polyethylene (UHMW PE) having an anisotropic morphology comprising:

heating an original powder stock or a partially fused, melt-crystallized stock of UHMW PE as defined by ASTM D 4020-81 having granular memory, at a temperature of 320° C in the absence of oxygen at a compression pressure of about 20-50 MPa for about ten minutes, then at about 150° C placing the material under a compression pressure of about 70-280 MPa for another ten minutes to provide a melt in which the stock fuses completely and loses memory of its former granular structure,

cooling the resultant material to ambient temperature under a compression pressure of about 20 MPa to give a UHMW PE having a semicrystalline morphology which has no memory of the granular nature of the original stock, and

extruding the semicrystalline product through an extrusion rolling die at a tempera-

ture of about 130° C at a deformation ratio of about 5 to 8.

10. A method for making an ultra-high-molecular-weight polyethylene having an anisotropic morphology comprising:

heating an original powder stock or a partially fused, melt-crystallized stock of UHMW PE as defined by ASTM D 4020-81 having a granular memory, at a temperature of 320° C in the absence of oxygen at a compression pressure of about 20-50 MPa for about ten minutes,

then at about 150° C placing the material under a compression pressure of about 70-280 MPa for another ten minutes to provide a melt in which the stock fuses completely and loses memory of its former granular structure,

cooling the resultant material to ambient temperatures under a compression pressure of about 20 MPa to give a UHMW PE having a semicrystalline morphology which has no memory of the granular nature of the original stock, and

drawing the semicrystalline product at a temperature of about 130° C at a deformation ratio of about 5 to 8.

11. An ultra-high-molecular-weight polyethylene (UHMW PE) having isotropic semicrystalline morphology obtained from a completely fused UHMW PE as defined by ASTM D 4020-81 without any memory of a granular structure.

12. An ultra-high-molecular-weight polyethylene (UHMW PE) having isotropic semi-crystalline morphology obtained from a homogeneous melt of UHMW PE as defined by ASTM D 4020-81 without the aid of radiation dopants.

13. A homogeneous melt crystallized ultra-high molecular-weight polyethylene having

an isotropic semicrystalline morphology with a molecular network structure and physical entanglements obtained from an UHMW PE as defined by ASTM D 4020-81 without the aid of radiation cross-linking and chemical cross-linking agents.

14. An ultra-high-molecular-weight polyethylene (UHMW PE) useful for the fabrication of an orthopaedic prosthetic device or a tendon having a molecular weight of several millions and made by

first heating an original powder stock or a partially fused, melt-crystallized stock of UHMW PE as defined by ASTM D 4020-81 having a granular memory, to a temperature

between 220 and 320° C in the absence of oxygen to fuse the stock completely and lose memory of its former granular structure, and

then cooling the resultant material to ambient temperatures under compression load to give a UHMW PE having a semicrystalline morphology without memory of the granular nature of the original stock.

15. An ultra-high-molecular-weight polyethylene (UHMW PE) having anisotropic morphology comprising:

a solid-state deformed UHMW PE of UHMW PE as defined by ASTM D 4020-81 having semicrystalline morphology and having no memory of a granular nature, deformed at a temperature near but below its crystalline melting point at a deformation ratio of about 5 to 8.

16. The anisotropic ultra-high-molecular-weight polyethylene of claim 15 wherein the solid state deformed UHMW PE has a filamentary or ribbon-like morphology.

17. The anisotropic ultra-high-molecular-weight polyethylene of claim 16 wherein the filamentary or ribbon-like products exhibit resistance to fibrillation without the aid of radiation cross-linking or chemical cross-linking agents.

18. An ultra-high-molecular-weight polyethylene (UHMW PE) useful for tendon fabrication, having a molecular weight of several millions and made by

first heating an original powder stock or a partially fused, melt-crystallized stock of UHMW PE as defined by ASTM D 4020-81 having a granular memory, to a temperature between 220 and 320° C in the absence of oxygen to fuse the stock completely and lose memory of its former granular structure,

then cooling the resultant material to ambient temperatures under compression load to give a UHMW PE having a semicrystalline morphology without memory of the granular nature of the original stock, and

then extruding the semicrystalline product through an extrusion rolling die at a temperature of about 130° C and at a deformation ratio of about 5-8.

19. An ultra-high-molecular-weight polyethylene (UHMW PE) useful for tendon fabrication, having a molecular weight of several millions and made by

first heating an original powder stock or a partially fused, melt-crystallized stock of UHMW PE as defined by ASTM D 4020-81

having a granular memory, to a temperature between 220 and 320° C in the absence of oxygen to fuse the stock completely and lose memory of its former granular structure,

then cooling the resultant material to ambient temperatures under compression load to give a UHMW PE having a semicrystalline morphology without memory of the granular nature of the original stock, and

then drawing the semicrystalline product at a temperature of about 130° C and at a deformation ratio of about 5-8.

20. An ultra-high-molecular-weight polyethylene (UHMW PE) useful for the fabrication of an orthopaedic prosthetic device, having a molecular weight of several millions and made by

first heating an original powder stock or a partially fused, melt-crystallized stock of UHMW PE as defined by ASTM D 4020-81 having a granular memory, to a temperature between 220 and 320°C in the absence of oxygen to fuse the stock completely and lose memory of its former granular structure,

then cooling the resultant material to ambient temperatures under compresssion load to give a UHMW PE having a semicrystalline morphology without memory of the granular nature of the original stock, and

then deforming the semicrystalline product at a temperature of about 130°C and at a deformation ratio of about 5 - 8.

21. A method for making an ultra-high-molecular-weight polyethylene (UHMW PE) having an isotropic homogeneous semicrystalline morphology comprising:

heating an original powder stock or a partially fused melt-crystallized stock of UHMW PE as defined by ASTM D 4020-81 having granular memory, to a temperature between 220° C and 320° C in the absence of oxygen at a pressure of about 20-50 MPa to fuse the stock completely to form a homogeneous melt which loses memory of its former granular structure, and

then at about 150° C placing the material under a pressure of about 70-280 MPa for another ten minutes to provide a melt in which the stock fuses completely and loses memory of its former granular structure, and

cooling the resultant material to ambient temperature under a pressure of about 20 MPa to give a UHMW PE having a semicrystalline morphology which has no memory of the granular nature of the original stock.

22. A method for making an ultra-high-molecular-

weight polyethylene (UHMW PE) having an anisotropic morphology comprising:

heating an original powder stock or a partially fused, melt-crystallized stock of UHMW PE as defined by ASTM D 4020-81 having granular memory, to a temperature between 220° C and 320° C in the absence of oxygen at a compression pressure of about 20-50 MPa to fuse the stock completely to form a homogeneous melt which loses memory of its former granular structure, and

then at about 150° C placing the material under a compression pressure of about 70-280 MPa for another ten minutes to provide a melt in which the stock fuses completely and loses memory of its former granular structure,

cooling the resultant material to ambient temperature under a compression pressure of about 20 MPa to give a UHMW PE having a semicrystalline morphology which has no memory of the granular nature of the original stock, and

extruding the semicrystalline product through an extrusion rolling die at a temperature of about 130° C at a deformation ratio of about 5 to 8.

23. A method for making an ultra-high-molecular-weight polyethylene having an anisotropic morphology comprising:

heating an original powder stock or a partially fused, melt-crystallized stock of UHMW PE as defined by ASTM D 4020-81 having a granular memory, to a temperature between 220° C and 320° C in the absence of oxygen at a compression pressure of about 20-50 MPa to fuse the stock completely to form a homogeneous melt which loses memory of its former granular structure, and

then at about 150° C placing the material under a compression pressure of about 70-280 MPa for another ten minutes to provide a melt in which the stock fuses completely and loses memory of its former granular structure,

cooling the resultant material to ambient temperatures under a compression pressure of about 20 MPa to give a UHMW PE having a semicrystalline morphology which has no memory of the granular nature of the original stock, and

drawing the semicrystalline product at a temperature of about 130° C at a deformation ratio of about 5 to 8.

Revendications

1. Procédé de fabrication d'un polyéthylène à masse moléculaire ultra-haute (PEMMUH), pré-

sentant une morphologie semi-cristalline isotrope, ledit procédé comprenant:

le chauffage d'une charge initiale pulvérulente, ou cristallisée en fusion et partiellement fondue, de PEMMUH tel que défini par ASTM D-4020-81, présentant une mémoire granulaire, à une température de 220 à 320°C, en l'absence d'oxygène, de façon à faire fondre la charge complètement pour former une masse fondue homogène qui perd la mémoire de sa structure granulaire antérieure, et

le refroidissement de la masse fondue résultante jusqu'à la température ambiante, sous compression, pour former un PEMMUH présentant un morphologie semi-cristalline isotrope homogène et qui n'a pas de mémoire de la nature granulaire de la charge initiale.

2. Procédé de la revendication 1, dans lequel l'étape de chauffage comporte un chauffage à 320°C pendant 10 minutes environ.

3. Procédé de fabrication d'un polyéthylène à masse moléculaire ultra-haute (PEMMUH), présentant une morphologie semi-cristalline isotrope homogène, ledit procédé comprenant:

le chauffage d'une charge initiale pulvérulente, ou cristallisée en fusion et partiellement fondue, de PEMMUH tel que défini par ASTM D-4020-81, présentant une mémoire granulaire, à une température de 320°C, en l'absence d'oxygène, sous une pression d'environ 20 à 50 MPa pendant environ 10 minutes,

puis, à environ 150°C, la mise du matériau sous une pression d'environ 70 à 280 MPa pendant 10 minutes supplémentaires, ce qui donne une masse fondue dans laquelle la charge fond complètement et perd la mémoire de sa structure granulaire antérieure, et

le refroidissement de la matière résultante jusqu'à la température ambiante, sous pression d'environ 20 MPa, pour former un PEMMUH présentant une morphologie semi-cristalline et qui n'a pas de mémoire de la nature granulaire de la charge initiale.

4. Procédé de fabrication d'un polyéthylène à masse moléculaire ultra-haute (PEMMUH), présentant une morphologie anisotrope, ledit procédé comprenant:

le chauffage d'une charge initiale pulvérulente, ou cristallisée en fusion et partiellement fondue, de PEMMUH tel que défini par ASTM D-4020-81, présentant une mémoire granulaire, à une température de 220 à 320°C, en l'absence d'oxygène, de façon à faire fondre la charge complètement pour qu'elle perde la mémoire de sa structure granulaire antérieure,

le refroidissement de la matière résultante jusqu'à la température ambiante, sous compression, pour former un PEMMUH présentant une morphologie semi-cristalline isotrope homogène initiale et qui n'a pas de mémoire de la nature granulaire de la charge initiale, et

la déformation à l'état solide de ce PEMMUH semi-cristallin, avec un rapport de déformation d'environ 5 à 8, à une température proche de son point de fusion à l'état cristallin, mais inférieure à ce point.

5. Procédé de la revendication 4, dans lequel la température à laquelle est effectuée la déformation vaut environ 130°C.

6. Procédé de la revendication 4, dans lequel le chauffage s'accompagne d'une compression sous une pression d'environ 20 à 50 MPa.

7. Procédé de la revendication 6, dans lequel l'étape de chauffage comprend également un chauffage à 150°C sous une pression d'environ 70 à 280 MPa.

8. Procédé de la revendication 4, dans lequel l'étape de déformation comprend un étirage à un rapport valant au moins 5.

9. Procédé de fabrication d'un polyéthylène à masse moléculaire ultra-haute (PEMMUH), présentant une morphologie anisotrope, ledit procédé comprenant:

le chauffage d'une charge initiale pulvérulente, ou cristallisée en fusion et partiellement fondue, de PEMMUH tel que défini par ASTM D- 4020-81, présentant une mémoire granulaire, à une température de 320°C, en l'absence d'oxygène, sous une pression de compression d'environ 20 à 50 MPa pendant environ 10 minutes,

puis, à environ 150°C, la mise du matériau sous une pression de compression d'environ 70 à 280 MPa pendant 10 minutes supplémentaires, ce qui donne une masse fondue dans laquelle la charge fond complètement et perd la mémoire de sa structure granulaire antérieure,

le refroidissement de la matière résultante jusqu'à la température ambiante, sous une pression de compression d'environ 20 MPa, pour former un PEMMUH présentant un morphologie semi-cristalline et qui n'a pas de mémoire de la nature granulaire de la charge initiale, et

l'extrusion de ce produit semi-cristallin dans une extrudeuse - calandre, à une température d'environ 130°C, avec un rapport de

déformation d'environ 5 à 8.

10. Procédé de fabrication d'un polyéthylène à masse moléculaire ultra-haute (PEMMUH), présentant une morphologie anisotrope, ledit procédé comprenant:

le chauffage d'une charge initiale pulvérulente, ou cristallisée en fusion et partiellement fondue, de PEMMUH tel que défini par ASTM D-4020-81, présentant une mémoire granulaire, à une température de 320°C, en l'absence d'oxygène, sous une pression de compression d'environ 20 à 50 MPa pendant environ 10 minutes,

puis, à environ 150°C, la mise du matériau sous une pression de compression d'environ 70 à 280 MPa pendant 10 minutes supplémentaires, ce qui donne une masse fondue dans laquelle la charge fond complètement et perd la mémoire de sa structure granulaire antérieure,

le refroidissement de la masse fondue résultante jusqu'à la température ambiante, sous une pression de compression d'environ 20 MPa, pour former un PEMMUH présentant un morphologie semi-cristalline et qui n'a pas de mémoire de la nature granulaire de la charge initiale, et

l'étirage du produit semi-cristallin à une température d'environ 130°C et avec un rapport de déformation d'environ 5 à 8.

11. Polyéthylène à masse moléculaire ultra-haute (PEMMUH) présentant une morphologie semi-cristalline isotrope, obtenue à partir d'un PEMMUH, tel que défini par ASTM D-4020-81, complètement fondu, ne présentant aucune mémoire de sa structure granulaire.

12. Polyéthylène à masse moléculaire ultra-haute (PEMMUH) présentant une morphologie semi-cristalline isotrope, obtenue à partir d'une masse homogène fondue de PEMMUH, tel que défini par ASTM D-4020-81, sans l'aide de dopants par radiation.

13. Polyéthylène à masse moléculaire ultra-haute, homogène, cristallisé en fusion, présentant une morphologie semi-cristalline isotrope, avec une structure moléculaire réticulée et des enchevêtrements physiques, et obtenu à partir d'un PEMMUH tel que défini par ASTM D-4020-81, sans recours à une réticulation par irradiation ou à des agents chimiques de réticulation.

14. Polyéthylène à masse moléculaire ultra-haute (PEMMUH), utile pour la fabrication d'un dispositif de prothèse orthopédique ou d'un tendon,

présentant une masse moléculaire de plusieurs millions et fabriqué par

chauffage d'une charge initiale pulvérulente, ou cristallisée en fusion et partiellement fondue, de PEMMUH tel que défini par ASTM D-4020-81, présentant une mémoire granulaire, à une température de 220 à 320°C, en l'absence d'oxygène, de façon à faire fondre la charge complètement pour qu'elle perde la mémoire de sa structure granulaire antérieure, et

le refroidissement de la matière résultante jusqu'à la température ambiante, sous compression, pour former un PEMMUH présentant une morphologie semi-cristalline et qui n'a pas de mémoire de la nature granulaire de la charge initiale.

15. Polyéthylène à masse moléculaire ultra-haute (PEMMUH), présentant une morphologie anisotrope et comprenant:

un PEMMUH, tel que défini par ASTM D-4020-81, présentant une morphologie semi-cristalline et n'ayant pas de mémoire d'une nature granulaire, et déformé à l'état solide à une température proche de son point de fusion à l'état cristallin, mais inférieure à ce point, avec un rapport de déformation d'environ 5 à 8.

16. Polyéthylène à masse moléculaire ultra-haute et anisotrope de la revendication 15, dans lequel le PEMMUH déformé à l'état solide présente une morphologie de filament ou de ruban.

17. Polyéthylène à masse moléculaire ultra-haute et anisotrope de la revendication 16, dans lequel les produits en forme de filaments ou de rubans présentent une résistance à la fibrillation, sans que l'on ait recours à une réticulation par irradiation ou à des agents chimiques de réticulation.

18. Polyéthylène à masse moléculaire ultra-haute (PEMMUH), utile pour la fabrication d'un tendon, présentant une masse moléculaire de plusieurs millions et fabriqué par

chauffage d'une charge initiale pulvérulente, ou cristallisée en fusion et partiellement fondue, de PEMMUH tel que défini par ASTM D-4020-81, présentant une mémoire granulaire, à une température de 220 à 320°C, en l'absence d'oxygène, de façon à faire fondre la charge complètement pour qu'elle perde la mémoire de sa structure granulaire antérieure, et

le refroidissement de la matière résultante

jusqu'à la température ambiante, sous compression, pour former un PEMMUH présentant une morphologie semi-cristalline et qui n'a pas de mémoire de la nature granulaire de la charge initiale, et

l'extrusion du produit semi-cristallin dans une extrudeuse - calandre, à une température d'environ 130°C et avec un rapport de déformation d'environ 5 à 8.

19. Polyéthylène à masse moléculaire ultra-haute (PEMMUH), utile pour la fabrication d'un tendon, présentant une masse moléculaire de plusieurs millions et fabriqué par

chauffage d'une charge initiale pulvérulente, ou cristallisée en fusion et partiellement fondue, de PEMMUH tel que défini par ASTM D-4020-81, présentant une mémoire granulaire, à une température de 220 à 320°C, en l'absence d'oxygène, de façon à faire fondre la charge complètement pour qu'elle perde la mémoire de sa structure granulaire antérieure,

le refroidissement de la matière résultante jusqu'à la température ambiante, sous compression, pour former un PEMMUH présentant un morphologie semi-cristalline et qui n'a pas de mémoire de la nature granulaire de la charge initiale, et

l'étirage du produit semi-cristallin, à une température d'environ 130°C et avec un rapport de déformation d'environ 5 à 8.

20. Polyéthylène à masse moléculaire ultra-haute (PEMMUH), utile pour la fabrication d'un dispositif de prothèse orthopédique, présentant une masse moléculaire de plusieurs millions et fabriqué par

chauffage d'une charge initiale pulvérulente, ou cristallisée en fusion et partiellement fondue, de PEMMUH tel que défini par ASTM D-4020-81, présentant une mémoire granulaire, à une température de 220 à 320°C, en l'absence d'oxygène, de façon à faire fondre la charge complètement pour qu'elle perde la mémoire de sa structure granulaire antérieure,

le refroidissement de la matière résultante jusqu'à la température ambiante, sous compression, pour former un PEMMUH présentant une morphologie semi-cristalline et qui n'a pas de mémoire de la nature granulaire de la charge initiale, et

la déformation du produit semi-cristallin à une température d'environ 130°C et avec un rapport de déformation d'environ 5 à 8.

21. Procédé de fabrication d'un polyéthylène à masse moléculaire ultra-haute (PEMMUH), présentant une morphologie semi-cristalline isotro-

pe homogène, ledit procédé comprenant:

le chauffage d'une charge initiale pulvérulente, ou cristallisée en fusion et partiellement fondue, de PEMMUH tel que défini par ASTM D-4020-81, présentant une mémoire granulaire, à une température de 220 à 320°C, en l'absence d'oxygène, sous une pression d'environ 20 à 50 MPa, de façon à faire fondre la charge complètement pour former une masse fondue homogène qui perd la mémoire de sa structure granulaire antérieure,

puis, à environ 150°C, la mise du matériau sous une pression d'environ 70 à 280 MPa pendant 10 minutes supplémentaires, ce qui donne une masse fondue dans laquelle la charge fond complètement et perd la mémoire de sa structure granulaire antérieure, et

le refroidissement de la matière résultante jusqu'à la température ambiante, sous pression d'environ 20 MPa, pour former un PEMMUH présentant un morphologie semi-cristalline et qui n'a pas de mémoire de la nature granulaire de la charge initiale.

22. Procédé de fabrication d'un polyéthylène à masse moléculaire ultra-haute (PEMMUH), présentant une morphologie anisotrope, ledit procédé comprenant:

le chauffage d'une charge initiale pulvérulente, ou cristallisée en fusion et partiellement fondue, de PEMMUH tel que défini par ASTM D-4020-81, présentant une mémoire granulaire, à une température de 220 à 320°C, en l'absence d'oxygène, sous une pression de compression d'environ 20 à 50 MPa, de façon à faire fondre la charge complètement pour former une masse fondue homogène qui perd la mémoire de sa structure granulaire antérieure,

puis, à environ 150°C, la mise du matériau sous une pression de compression d'environ 70 à 280 MPa pendant 10 minutes supplémentaires, ce qui donne une masse fondue dans laquelle la charge fond complètement et perd la mémoire de sa structure granulaire antérieure, et

le refroidissement de la matière résultante jusqu'à la température ambiante, sous une pression de compression d'environ 20 MPa, pour former un PEMMUH présentant un morphologie semi-cristalline et qui n'a pas de mémoire de la nature granulaire de la charge initiale, et

l'extrusion du produit semi-cristallin dans une extrudeuse - calandre, à une température d'environ 130°C et avec un rapport de déformation d'environ 5 à 8.

23. Procédé de fabrication d'un polyéthylène à

masse moléculaire ultra-haute, PEMMUH, présentant une morphologie anisotrope, ledit procédé comprenant:

le chauffage d'une charge initiale pulvérulente, ou cristallisée en fusion et partiellement fondue, de PEMMUH tel que défini par ASTM D- 4020-81, présentant une mémoire granulaire, à une température de 220 à 320°C, en l'absence d'oxygène, sous une pression de compression d'environ 20 à 50 MPa, de façon à faire fondre la charge complètement pour former une masse fondue homogène qui perd la mémoire de sa structure granulaire antérieure,

puis, à environ 150°C, la mise du matériau sous une pression de compression d'environ 70 à 280 MPa pendant 10 minutes supplémentaires, ce qui donne une masse fondue dans laquelle la charge fond complètement et perd la mémoire de sa structure granulaire antérieure,

le refroidissement de la matière résultante jusqu'à la température ambiante, sous une pression de compression d'environ 20 MPa, pour former un PEMMUH présentant un morphologie semi-cristalline et qui n'a pas de mémoire de la nature granulaire de la charge initiale, et

l'étirage du produit semi-cristallin, à une température d'environ 130°C et avec un rapport de déformation d'environ 5 à 8.

Patentansprüche

1. Verfahren zur Herstellung eines Polyethylens mit ultrahohem Molekulargewicht (UHMW PE) mit einer isotropen, semi-kristallinen Morphologie, umfassend:

Erhitzen eines ursprünglichen Pulverausgangsmaterials oder eines partiell geschmolzenen, schmelz-kristallisierten Ausgangsmaterials aus UHMW PE entsprechend der Definition ASTM D 4020-81 mit einem Granulatgedächtnis auf eine Temperatur von 220-320°C bei Abwesenheit von Sauerstoff zum vollständigen Schmelzen des Ausgangsmaterials unter Bildung einer homogenen Schmelze, welche das Gedächtnis für ihre frühere Granulatstruktur verliert und

Abkühlen der erhaltenen Schmelze auf Umgebungstemperaturen unter Kompression zur Bildung eines UHMW PE mit einer homogenen isotropen, semi-kristallinen Morphologie, welches kein Gedächtnis für die Granulatnatur des ursprünglichen Ausgangsmaterials besitzt.

2. Verfahren nach Anspruch 1, worin die Erhitzungsstufe das Erhitzen auf 320°C für etwa 10

Minuten umfaßt.

3. Verfahren zur Herstellung eines Polyethylens mit ultrahohem Molekulargewicht (UHMW PE) mit einer isotropen, homogenen, semi-kristallinen Morphologie, umfassend:

Erhitzen eines ursprünglichen Pulverausgangsmaterials oder eines partiell geschmolzenen, schmelz-kristallisierten Ausgangsmaterials aus UHMW PE entsprechend der Definition ASTM D 4020-81 mit einem Granulatgedächtnis auf eine Temperatur von 320°C bei Abwesenheit von Sauerstoff bei einem Druck von etwa 20-50 MPa für etwa 10 Minuten,

dann bei etwa 150°C Setzen des Materials unter einen Druck von etwa 70-280 MPa für weitere 10 Minuten zur Bereitstellung einer Schmelze, in welcher das Ausgangsmaterial vollständig schmilzt und das Gedächtnis für seine frühere Granulatstruktur verliert, und

Abkühlen des erhaltenen Materials auf Umgebungstemperatur unter einem Druck von etwa 20 MPa zur Bildung eines UHMW PE mit einer semikristallinen Morphologie, welches kein Gedächtnis für die Granulatnatur des ursprünglichen Ausgangsmaterials besitzt.

4. Verfahren zur Herstellung eines Polyethylens mit ultrahohem Molekulargewicht (UHMW PE) mit einer anisotropen Morphologie, umfassend:

Erhitzen eines ursprünglichen Pulverausgangsmaterials oder eines partiell geschmolzenen, schmelz-kristallisierten Ausgangsmaterials von UHMW PE entsprechend der Definition ASTM D 4020-81 mit Granulatgedächtnis auf eine Temperatur zwischen 220 und 320°C in Abwesenheit von Sauerstoff zum vollständigen Schmelzen des Ausgangsmaterials und zum Verlust seiner ursprünglichen Granulatstruktur,

Abkühlen des erhaltenen Materials auf Umgebungstemperatur unter Druck zur Bereitstellung eines UHMW PE mit einer anfänglichen homogenen isotropen, semi-kristallinen Morphologie, welches kein Gedächtnis der Granulatnatur des ursprünglichen Ausgangsmaterials besitzt, und

Verformung im festen Zustand dieses semi-kristallinen UHMW PE bei einer Temperatur nahe bei, jedoch unterhalb seines kristallinen Schmelzpunktes bei einem Verformungsverhältnis von etwa 5 bis 8.

5. Verfahren nach Anspruch 4, worin die Verformungstemperatur etwa 130°C beträgt.

6. Verfahren nach Anspruch 4, worin das Erhitzen von einem Kompressionsdruck von etwa 20-50 MPa begleitet ist.

7. Verfahren nach Anspruch 6, worin die Erhit-
zungsstufe ebenfalls Wärme bei 150°C unter
einem Druck von etwa 70-280 MPa einschließt.

8. Verfahren nach Anspruch 4, worin die Verfor-
mungsstufe das Ziehen um wenigstens das 5-
fache einschließt.

9. Verfahren zur Herstellung eines Polyethylens
mit ultrahohem Molekulargewicht (UHMW PE)
mit einer anisotropen Morphologie, umfassend:

Erhitzen eines ursprünglichen Pulveraus-
gangsmaterials oder eines partiell geschmolze-
nen, schmelz-kristallisierten Ausgangsmaterials
von UHMW PE entsprechend der Definition
ASTM D 4020-81, das Granulatgedächtnis be-
sitzt, auf eine Temperatur von 320°C in Abwe-
senheit von Sauerstoff bei einem Kompres-
sionsdruck von etwa 20-50 MPa für etwa 10
Minuten,

dann bei etwa 150°C Setzen des Materi-
als unter einen Kompressionsdruck von etwa
70-280 MPa für weitere 10 Minuten zur Bereit-
stellung einer Schmelze, in welcher das Aus-
gangsmaterial vollständig schmilzt und das
Gedächtnis für seine frühere Granulatstruktur
verliert,

Abkühlen des erhaltenen Materials auf
Umgebungstemperatur unter einem Kompres-
sionsdruck von etwa 20 MPa zum Erhalt eines
UHMW PE mit einer semi-kristallinen Morpho-
logie, welche kein Gedächtnis der Granulatna-
tur des ursprünglichen Ausgangsmaterials be-
sitzt, und

Extrudieren des semi-kristallinen Produk-
tes durch ein Extrusionswalzwerkzeug bei ei-
ner Temperatur von etwa 130°C bei einem
Verformungsverhältnis von etwa 5 bis 8.

10. Verfahren zur Herstellung eines Polyethylens
mit ultrahohem Molekulargewicht mit anisotro-
per Morphologie, umfassend:

Erhitzen eines ursprünglichen Pulveraus-
gangsmaterials oder eines partiell geschmolze-
nen, schmelz-kristallisierten Ausgangsmaterials
aus UHMW PE entsprechend der Definition
ASTM D 4020-81, das ein Granulatgedächtnis
besitzt, auf eine Temperatur von 320°C in
Abwesenheit von Sauerstoff bei einem Kom-
pressionsdruck von etwa 20-50 MPa für etwa
10 min,

dann bei etwa 150°C Setzen des Materi-
als unter einem Kompressionsdruck von etwa
70-280 MPa für weitere 10 Minuten zur Bereit-
stellung einer Schmelze, in welcher das Aus-
gangsmaterial vollständig schmilzt und das
Gedächtnis für seine frühere Granulatstruktur
verliert,

Abkühlen des erhaltenen Materials auf
Umgebungstemperaturen unter einem Kom-
pressionsdruck von etwa 20 MPa zum Erhalt
eines UHMW PE mit einer semi-kristallinen
Morphologie, das kein Gedächtnis der Granu-
latnatur des ursprünglichen Ausgangsmaterials
besitzt, und

Ziehen des semi-kristallinen Produktes bei
einer Temperatur von etwa 130°C bei einem
Verformungsverhältnis von etwa 5 bis 8.

11. Polyethylen mit ultrahohem Molekulargewicht
(UHMW PE) mit isotroper, semi-kristalliner
Morphologie, erhalten aus einem vollständig
geschmolzenen UHMW PE entsprechend der
Definition der ASTM D 4020-81 ohne irgendein
Gedächtnis einer Granulatstruktur.

12. Polyethylen mit ultrahohem Molekulargewicht
(UHMW PE) mit isotroper, semi-kristalliner
Morphologie, erhalten aus einer homogenen
Schmelze von UHMW PE entsprechend der
Definition der ASTM D 4020-81 ohne Zuhilfe-
nahme von Strahlungsdotierungsmitteln.

13. Homogenes, schmelz-kristallisiertes Polyeth-
ylen mit ultrahohem Molekulargewicht, besit-
zend:

eine isotrope, semi-kristalline Morphologie
mit einer molekularen Netzwerkstruktur und
physikalischen Verwirrungen, erhalten aus ei-
nem UHMW PE entsprechend der Definition
der ASTM D 4020-81 ohne Zuhilfenahme von
strahlungs-vernetzenden und chemisch-vernet-
zenden Mitteln.

14. Polyethylen mit ultrahohem Molekulargewicht
(UHMW PE), brauchbar für die Herstellung ei-
nes orthopädischen, prothetischen Teiles oder
einer Sehne mit einem Molekulargewicht von
mehreren Millionen und hergestellt durch:

zuerst Erhitzen eines ursprünglichen Pul-
verausgangsmaterials oder eines partiell ge-
schmolzenen, schmelzkristallisierten Aus-
gangsmaterials aus UHMW PE entsprechend
der Definition der ASTM D 4020-81, das ein
Granulatgedächtnis besitzt, auf eine Tempera-
tur zwischen 220 und 320°C in Abwesenheit
von Sauerstoff zum vollständigen Schmelzen
des Ausgangsmaterials und zum Verlust des
Gedächtnisses seiner früheren Granulatstruk-
tur, und

dann Abkühlen des erhaltenen Materials
auf Umgebungstemperaturen unter Kompres-
sionsbelastung zum Erhalt eines UHMW PE
mit einer semi-kristallinen Morphologie ohne
Gedächtnis der Granulatnatur des ursprüngli-
chen Ausgangsmaterials.

15. Polyethylen mit ultrahohem Molekulargewicht (UHMW PE) mit anisotroper Morphologie, umfassend:

     ein festkörperverformtes UHMW PE aus UHMW PE entsprechend der Definition der ASTM D 4020-81 mit semi-kristalliner Morphologie und ohne Besitz eines Gedächtnisses einer Granulatnatur, verformt bei einer Temperatur nahe bei, jedoch unterhalb seines kristallinen Schmelzpunktes bei einem Verformungsverhältnis von etwa 5 bis 8.

16. Anisotropes Polyethylen mit ultrahohem Molekulargewicht nach Anspruch 15, worin das festkörperverformte UHMW PE eine fadenförmige oder bandähnliche Morphologie aufweist.

17. Anisotropes Polyethylen mit ultrahohem Molekulargewicht nach Anspruch 16, worin die fadenförmigen oder bandähnlichen Produkte gegenüber Fibrillierung Beständigkeit aufweisen ohne Zuhilfenahme von strahlungs-vernetzenden oder chemisch-vernetzenden Mitteln.

18. Polyethylen mit ultrahohem Molekulargewicht (UHMW PE), brauchbar zur Sehnenherstellung mit einem Molekulargewicht von mehreren Millionen und hergestellt durch:

     zuerst Erhitzen eines ursprünglichen Pulverausgangsmaterials oder eines partiell geschmolzenen, schmelzkristallisierten Ausgangsmaterials aus UHMW PE entsprechend der Definition der ASTM D 4020-81, das ein Granulatgedächtnis besitzt, auf eine Temperatur zwischen 220 und 320°C in Abwesenheit von Sauerstoff zum vollständigen Schmelzen des Ausgangsmaterials und zum Verlust des Gedächtnisses seiner früheren Granulatstruktur,

     dann Abkühlen des erhaltenen Materials auf Umgebungstemperaturen unter Kompressionsbelastung zur Bildung eines UHMW PE mit einer semi-kristallinen Morphologie ohne Gedächtnis der Granulatnatur des ursprünglichen Ausgangsmaterials, und

     dann Extrudieren des semi-kristallinen Produktes durch ein Extrusionswalzwerkzeug bei einer Temperatur von etwa 130°C und bei einem Verformungsverhältnis von etwa 5-8.

19. Polyethylen mit ultrahohem Molekulargewicht (UHMW PE), brauchbar zur Sehnenherstellung mit einem Molekulargewicht von mehreren Millionen und hergestellt durch:

     zuerst Erhitzen eines ursprünglichen Pulverausgangsmaterials oder eines partiell geschmolzenen, schmelzkristallisierten Ausgangsmaterials aus UHMW PE entsprechend

der Definition der ASTM D 4020-81, das ein Granulatgedächtnis besitzt, auf eine Temperatur zwischen 220 und 320°C in Abwesenheit von Sauerstoff zum vollständigen Schmelzen des Ausgangsmaterials und zum Verlust des Gedächtnisses seiner früheren Granulatstruktur,

     dann Abkühlen des erhaltenen Materials auf Umgebungstemperaturen unter Kompressionsbelastung zur Bildung eines UHMW PE mit einer semi-kristallinen Morphologie ohne Gedächtnis der Granulatnatur des ursprünglichen Ausgangsmaterials, und

     dann Ziehen des semi-kristallinen Produktes bei einer Temperatur von etwa 130°C und bei einem Verformungsverhältnis von etwa 5-8.

20. Polyethylen mit ultrahohem Molekulargewicht (UHMW PE), brauchbar zur Herstellung einer orthopädischen, prothetischen Teiles mit einem Molekulargewicht von mehreren Millionen und hergestellt durch:

     zuerst Erhitzen eines ursprünglichen Pulverausgangsmaterials oder eines partiell geschmolzenen, schmelzkristallisierten Ausgangsmaterials aus UHMW PE entsprechend der Definition der ASTM D 4020-81, das ein Granulatgedächtnis besitzt, auf eine Temperatur zwischen 220 und 320°C in Abwesenheit von Sauerstoff zum vollständigen Schmelzen des Ausgangsmaterials und zum Verlust des Gedächtnisses seiner früheren Granulatstruktur,

     dann Abkühlen des erhaltenen Materials auf Umgebungstemperaturen unter Kompressionsbelastung zur Bildung eines UHMW PE mit einer semi-kristallinen Morphologie ohne Gedächtnis der Granulatnatur des ursprünglichen Ausgangsmaterials, und

     dann Verformen des semi-kristallinen Produktes bei einer Temperatur von etwa 130°C und bei einem Verformungsverhältnis von etwa 5-8.

21. Verfahren zur Herstellung eines Polyethylens mit ultrahohem Molekulargewicht (UHMW PE) mit einer isotropen, homogenen, semi-kristallinen Morphologie, umfassend:

     Erhitzen eines ursprünglichen Pulverausgangsmaterials oder eines partiell geschmolzenen, schmelz-kristallisierten Ausgangsmaterials aus UHMW PE entsprechend der Definition der ASTM D 4020-81, das Granulatgedächtnis besitzt, auf eine Temperatur zwischen 220°C und 320°C in Abwesenheit von Sauerstoff bei einem Druck von etwa 20-50 MPa zum vollständigen Schmelzen des Ausgangsmaterials unter Bildung einer homogenen Schmelze,

welches das Gedächtnis seiner früheren Gra-
nulatstruktur verliert, und

    dann bei etwa 150°C Setzen des Materi-
als unter einen Druck von etwa 70-280 MPa für
weitere 10 min zur Bildung einer Schmelze, in
welcher das Ausgangsmaterial vollständig
schmilzt und das Gedächtnis seiner früheren
Granulatstruktur verliert, und

    Abkühlen des erhaltenen Materials auf
Umgebungstemperatur unter einem Druck von
etwa 20 MPa zur Bildung eines UHMW PE mit
einer semi-kristallinen Morphologie, welches
kein Gedächtnis der Granulatnatur des ur-
sprünglichen Ausgangsmaterials besitzt.

22. Verfahren zur Herstellung eines Polyethylens
    mit ultrahohem Molekulargewicht (UHMW PE)
    mit einer anisotropen Morphologie, umfassend:

    Erhitzen eines ursprünglichen Pulveraus-
gangsmaterials oder eines partiell geschmolze-
nen, schmelz-kristallisierten Ausgangsmaterials
aus UHMW PE entsprechend der Definition
der ASTM D 4020-81, das Granulatgedächtnis
besitzt, auf eine Temperatur zwischen 220°C
und 320°C in Abwesenheit von Sauerstoff bei
einem Kompressionsdruck von etwa 20-50
MPa zum vollständigen Schmelzen des Aus-
gangsmaterials unter Bildung einer homogenen
Schmelze, welches das Gedächtnis für seine
frühere Granulatstruktur verliert, und

    dann bei etwa 150°C Setzen des Materi-
als unter einen Kompressionsdruck von etwa
70-280 MPa für weitere 10 Minuten zur Bil-
dung einer Schmelze, in welcher das Aus-
gangsmaterial vollständig schmilzt und das
Gedächtnis seiner früheren Granulatstruktur
verliert,

    Abkühlen des erhaltenen Materials auf
Umgebungstemperatur unter einem Kompres-
sionsdruck von etwa 20 MPa zur Bildung eines
UHMW PE mit einer semi-kristallinen Morpho-
logie, welches kein Gedächtnis der Granulatna-
tur des ursprünglichen Ausgangsmaterials be-
sitzt, und

    Extrudieren des semi-kristallinen Produk-
tes durch ein Extrusionswalzwerkzeug bei ei-
ner Temperatur von etwa 130°C bei einem
Deformationsverhältnis von etwa 5 bis 8.

23. Verfahren zur Herstellung eines Polyethylens
    mit ultrahohem Molekulargewicht, das eine ani-
    sotrope Morphologie aufweist, umfassend:

    Erhitzen eines ursprünglichen Pulveraus-
gangsmaterials oder eines partiell geschmolze-
nen, schmelz-kristallisierten Ausgangsmaterials
aus UHMW PE entsprechend der Definition
der ASTM D 4020-81, das ein Granulatge-
dächtnis besitzt, auf eine Temperatur zwischen

220°C und 320°C in Abwesenheit von Sauer-
stoff bei einem Kompressionsdruck von etwa
20-50 MPa zum vollständigen Schmelzen des
Ausgangsmaterials unter Bildung einer homo-
genen Schmelze, welches das Gedächtnis sei-
ner früheren Granulatstruktur verliert, und

    dann bei etwa 150°C Setzen des Materi-
als unter einen Kompressionsdruck von etwa
70-280 MPa für weitere 10 Minuten zur Bil-
dung einer Schmelze, in welcher das Aus-
gangsmaterial vollständig schmilzt und das
Gedächtnis für seine frühere Granulatstruktur
verliert,

    Abkühlen des erhaltenen Materials auf
Umgebungstemperaturen unter einem Kom-
pressionsdruck von etwa 20 MPa zur Bildung
eines UHMW PE mit einer semi-kristallinen
Morphologie, das kein Gedächtnis der Granu-
latstruktur des ursprünglichen Ausgangsmateri-
als besitzt, und

    Ziehen des semi-kristallinen Produktes bei
einer Temperatur von etwa 130°c und bei
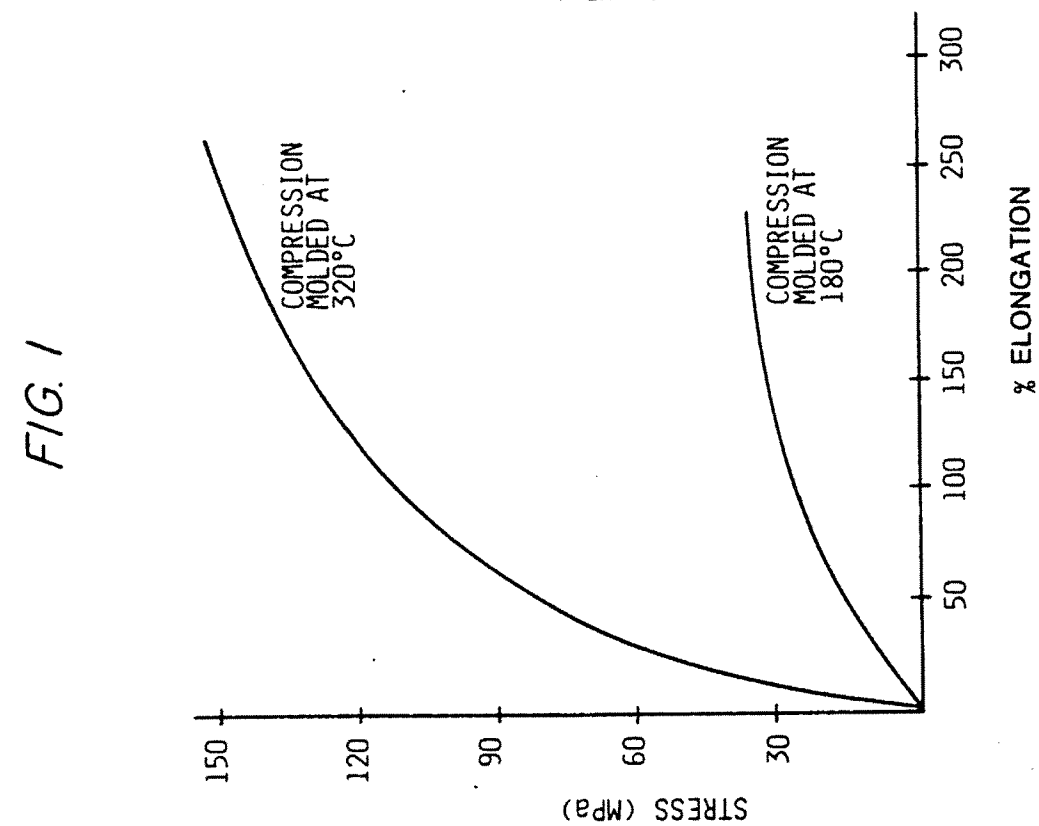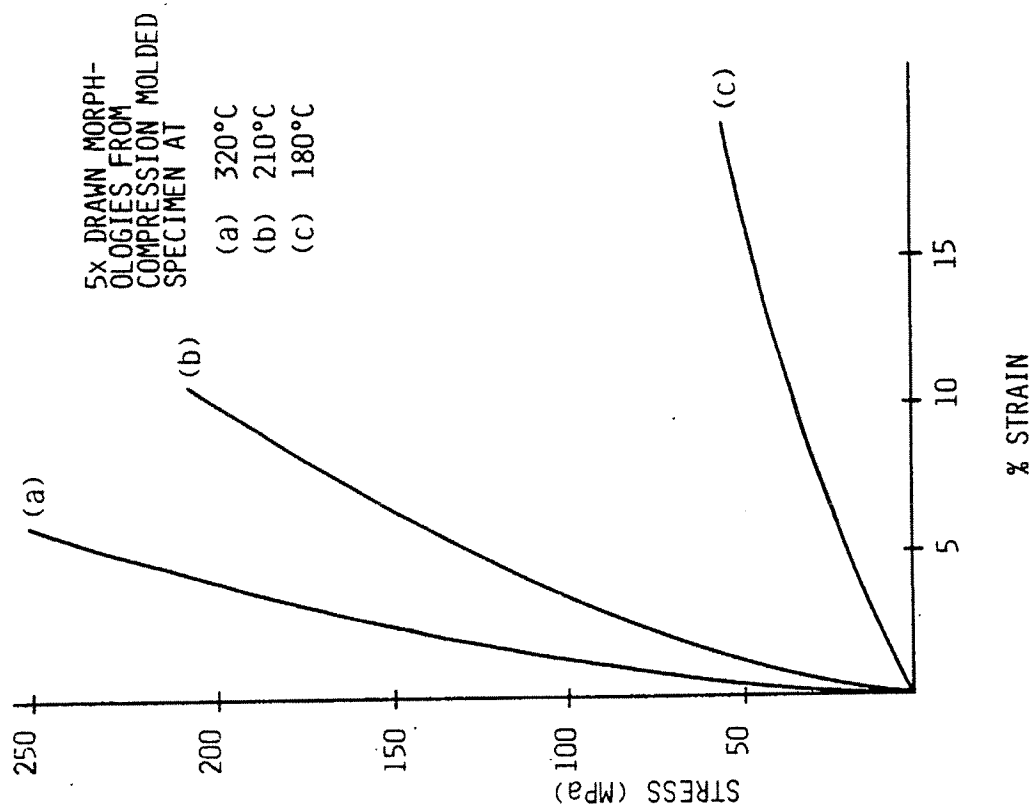einem Verformungsverhältnis von etwa 5 bis 8.

FIG. 2

5X DRAWN MORPH-
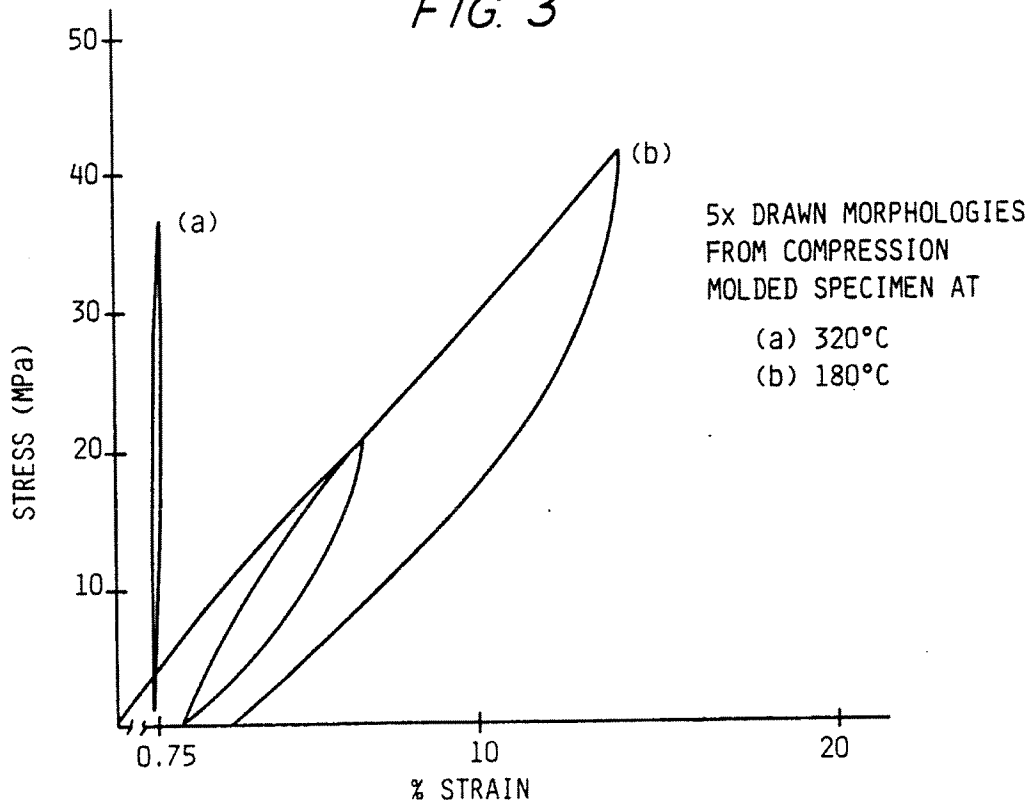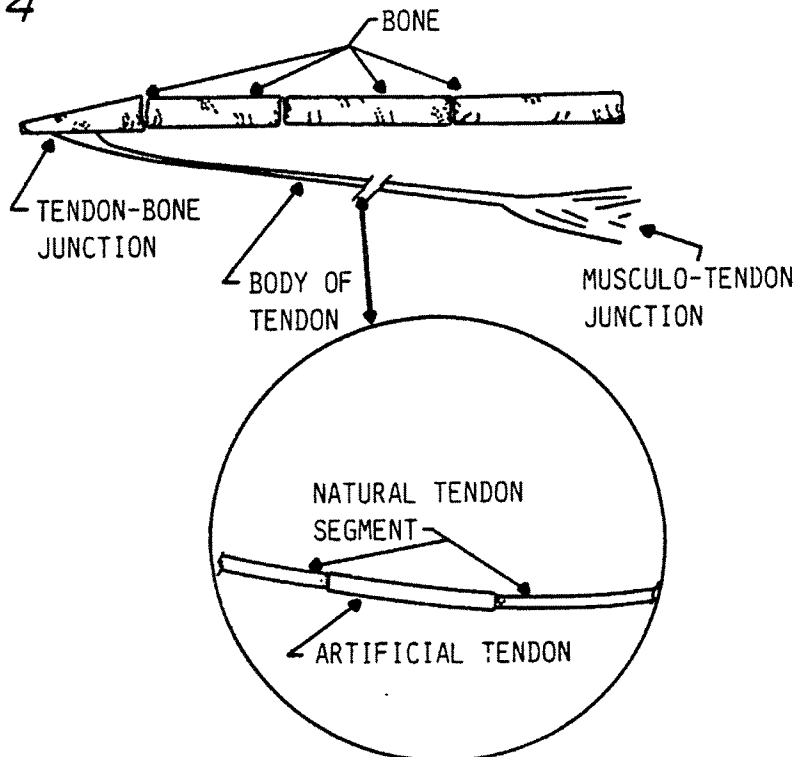OLOGIES FROM
COMPRESSION MOLDED
SPECIMEN AT

(a) 320°C
(b) 210°C
(c) 180°C

STRESS (MPa)

% STRAIN

FIG. 1

COMPRESSION
MOLDED AT
320°C

COMPRESSION
MOLDED AT
180°C

STRESS (MPa)

% ELONGATION

FIG. 3

5x DRAWN MORPHOLOGIES
FROM COMPRESSION
MOLDED SPECIMEN AT

  (a) 320°C
  (b) 180°C

FIG. 4

EUROPEAN PATENT SPECIFICATION

(54) Radiation-sterilized, packaged medical device.

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EP 0 218 003 B1

Description

The present invention relates to a radiation-sterilized medical device. More particularly, the present invention relates to a packaged medical device provided with a deodorizing means adapted to prevent emanation of an odor upon withdrawal of a radiation-sterilized medical device from a sterile containment bag.

As a method for sterilizing medical devices, sterilization with gamma-rays has been widely employed in recent years, particularly in the field of disposable medical devices. In order to maintain sterility up till the time of use, such a disposable medical device is generally sealed in a sterile bag and then sterilized with gamma-rays as pre-packaged in the bag. However, because of the presence of oxygen in the bag, irradiation with gamma-rays or other radiation excites the oxygen to yield ozone, an allotrope of oxygen, and, hence, generates the so-called gamma odor which is considered to be associated with ozone. This odor emanating upon unsealing of the sterile bag for removal of the medical device therefrom gives an uncomfortable sensation to the user of the device.

Furthermore, disposable medical devices are made, for the most part, of some plastic material or other and may suffer from decreased strength due to oxidation with time. Particularly in dry radiation-sterilization in a gaseous atmosphere where the surface of the plastic material is exposed to air, the presence of radiation-excited oxygen promotes oxidation of the plastic material with time at elevated temperatures so as to induce a decrease in strength.

In view of the problems mentioned hereinbefore, the present inventors conducted an intensive research and discovered that these problems all spring out from the presence of oxygen. Accordingly, they sought for means for elimination of oxygen.

FR-A 2 025 430 describes the packaging of a material such as foodstuff or catgut. The material is sterilized in the presence of an oxygen binding medium within a gas-tight package.

EP-A 111 062 describes a double package capable of being sterilized and can particularly be used for a prosthetic member. The package comprises two vat-like containers which are piled with each other with a lateral space surrounding the inner container. Each of the containers are closed with a covering whereby the inner container is provided with a support for laying down the prosthetic member. This double package is especially thought for enabling the operating personnel to take out the prosthetic member without any contamination.

The object of the present invention is to provide a dry radiation-sterilized medical equipment which does not give off an odor upon unsealing and is free from decreases in the strength of plastic parts thereof.

This and other objects of the invention will become apparent from the description hereinafter.

The present invention provides a packaged medical device comprising a medical device; a gas-permeable sterile bag containing the medical device therein; a wrapping member made of oxygen-impermeable material and wherein said medical device-containing bag, previously subjected to radiation-sterilization, is sealed; and deoxidizing agent contained in the wrapping member together with the medical device-containing bag.

Fig. 1 is a schematic illustration showing a packaged medical device in accordance with the present invention.

In the present invention, the radiation-sterilization is preferably sterilization with gamma-rays and the deoxidizing agent is preferably one based on activated iron oxide. The medical device to which the present invention can be applied with advantage includes a hollow fiber blood processing device, particularly a blood processing device employing a cellulose acetate hollow fiber membrane, which is generally believed to be incompatible with dry radiation-sterilization. The oxygen-impermeable material is preferably a laminated polyester-aluminum-polyethylene sheet.

According to the present invention, a medical device sealed in a sterile bag, after radiation-sterilization, is hermetically sealed in a wrapping member of oxygen-impermeable material together with a deoxidizing agent. For the reason, there is substantially no infiltration of oxygen from external environments and even the oxygen trapped in the course of the wrapping step is absorbed by the co-existing deoxidizing agent. Therefore, the inside of the wrapping member can be maintained in anoxic state so that the emanation of an odor and aging of the strength of the medical device can be successfully prevented.

Furthermore, since the sterile bag is a gas-permeable sterile bag, the oxygen and ozone present in the bag and the oxygen gradually released from the medical device are also instantly absorbed.

In addition, since the wrapping member is made of an oxygen-impermeable material, the entry of oxygen from the external environment is prevented almost completely and, therefore, an oxygen-free condition within the wrapping member can be maintained for a long time period.

An preferred embodiment of the present invention will now be described with reference to the accompanying drawing.

Referring to Fig. 1, a packaged medical device according to the present invention comprises a medical device 1 such as hollow fiber blood processing device, as sealed in a sterile bag 2 and further hermetically sealed, together with a deoxidizing agent 3, in a wrapping member 4. That is, the medical device 1 as such is first sealed in the sterile bag 2 and, then, after sterilization with gamma-rays, hermetically sealed into the wrapping member 4 together with the deoxidizing agent 3.

The sterile bag 2 is a gas-permeable sterile bag and the wrapping member 4 is made of an oxygen-impermeable material. The reason for using such a gas-permeable bag as the sterile bag is that if a gas-impermeable sterile bag be employed, even if sealing is made under oxygen-free conditions, the oxygen inherent in the medical device itself is gradually released and collects within the sterile bag and, as experience tells, the decrease in strength of the medical device is accelerated at elevated temperature.

In the invention, the term "sterile bag" is intended to mean a bag which is subjected to sterilization treatment in a state that a medical device is contained therein and through the wall of which bacteria cannot pass. The sterile bag may be gas-permeable over the entire surfaces thereof or in a part thereof.

Examples of the sterile bag include the followings: (1) A bag, both sides of which are made of a laminated polyester-polyethylene film and which has one or more gas-permeable parts where one or more openings such as slit are provided in the laminated film and the opening portions are covered with a polyethylene non-woven fabric or a wood-free paper. (2) A bag, one side of which is made of a wood-free paper or a polyethylene non-woven fabric, and the other side of which is made of a laminated polyester-polyethylene film. (3) A bag, both sides of which are made of a wood-free paper or a polyethylene non-woven fabric.

The reason for using a wrapping member made of an oxygen-impermeable material is to prevent infiltration of oxygen from external environments and, hence, to ensure a long efficacy life of the deoxidizing agent. Examples of the wrapping member used in the invention include a laminated sheet consisting of an exterior polyester film, an intermediate aluminum foil (or aluminum deposition layer) and an inner polyethylene film, a laminated sheet consisting of an exterior polyester film, an intermediate polyethylene film, an intermediate aluminum foil (or aluminum deposition layer) and an inner polyethylene film, a laminated sheet consisting of an exterior biaxially orientated polypropylene film, an intermediate ethylene-vinyl alcohol copolymer film and an inner polyethylene film, a laminated sheet consisting of an exterior vinylon film having a polyvinylidene chloride coating on both sides thereof and an inner polyethylene film, a laminated sheet consisting of an exterior biaxially orientated polyvinyl alcohol film and an inner polyethylene film, a laminated sheet consisting of an exterior polyvinylidene chloride-coated orientated polypropylene film and an inner polyethylene film, a laminated sheet consisting of an exterior polyvinylidene chloride-coated polyester film and an inner polyethylene film, a laminated sheet consisting of an exterior polyvinylidene chloride-coated oriented nylon film and an inner polyethylene film, a laminated sheet consisting of an exterior polyvinylidene chloride-coated cellophane and an inner polyethylene film, and a laminated sheet consisting of an exterior laminated high impact polystyrene-polyvinylidene chloride-polyethylene film and an inner non-oriented polypropylene film. From the standpoint of cost and efficiency, the most preferred examples of the oxygen-impermeable materials are a laminated sheet consisting of an exterior polyester film, an intermediate aluminum foil (or aluminum deposition layer) and an inner polyethylene film, and a laminated sheet consisting of an exterior polyester film, an intermediate polyethylene film, an intermediate aluminum foil (or aluminum deposition layer) and an inner polyethylene film.

The sterilization method may be any radiation-sterilization method, including one using gamma-rays and one utilizing electron beams. However, the present invention is more effective in case of sterilization with gamma-rays, which has a greater influence on the strength of the medical device, since the effect of the present invention which comprises sealing a medical device in an oxygen-impermeable wrapping member together with a deoxidizing agent is noticeably exhibited, especially when the problem of decreased strength of the medical device due to radiation-excited oxygen is taken into consideration.

The absorbed dose used in the radiation-sterilization varies depending upon the kind of medical device and the kind of radiation. In the case of sterilization of hollow fiber blood processing device with gamma-rays, an absorbed dose of 1.8 to 2.5 Mrad is usually used.

Because the deoxidizing agent is sealed together with a medical device contained in a gas-permeable sterile bag, it must be non-toxic. Moreover, the deoxidizing agent is preferably one which does not give rise to gases (hydrogen gas, carbon dioxide gas, and the like) upon absorption of oxygen. For these reasons, the deoxidizing agent is desirably one based on an active metal or metal compound and having its reaction rate, etc. controlled by a catalyst. The active metal or metal compound may for example be iron, zinc, copper or tin, or oxides of the foregoing metal but among the currently available deoxidizing agents, those based on activated iron oxide are most desirable. Among commercial deoxidizing agents of this type is Ageless (a commercial name of Mitsubishi Gas Chemical Company, Inc.). The deoxidizing agent is contained in a gas-permeable bag or container.

In the present invention, it is essential that, the medical device-containing bag is previously sterilized and then sealed together with a deoxidizing agent in an oxygen-impermeable wrapping member. That is, it must be avoided that a medical device is sealed together with a deoxidizing agent in a gas-impermeable bag and is subjected to radiation-sterilization in a state that the deoxidizing agent is present in the bag. The reason therefor is that when the medical device-containing bag is subjected to radiation sterilization in a state that a deoxidizing agent is present in the bag, the D value (which means the absorbed dose in which the number of bacteria is reduced to one-tenth time that before irradiation) is increased. This tendency is marked particularly in the case of a medical device using cellulose acetate hollow fiber, as shown in Example 4.

The tendency is also observed in the case of a medical device using silicone rubber hollow fiber.

As a method for removing the odor generated within the sterile bag, it might be contemplated to seal ac-

tive carbon as a deodorant together with the medical device but in view of the fact that this material oc-
cupies more than 10 times the volume of a typical deoxidizing agent, that its deodorizing efficiency is poor
at elevated temperature, and that it does not prevent the decrease of strenght with time, for instance,
the use of active carbon is not suitable for the purposes of the present invention.

5   Referring to the medical device to be packed according to the present invention, the method for inhib-
iting decrease of strength in accordance with the present invention, that is a method comprising sealing
a medical device contained in a gas-permeable sterile bag in an oxygen-impermeable wrapping member to-
gether with a deoxidizing agent after radiation-sterilization, can be applied to the radiation-sterilization
of any medical device basically made of a plastic material. For example, the present invention is of
10   course effective for a medical device such that its loss of strength will be confined within a tolerable
range even without provision of any specific means for preventing such decrease of strength. How-
ever, from the standpoint of cost and efficiency, the present invention can be preferably applied to hol-
low fiber blood processing devices, particularly to blood processing devices employing cellulose acetate
hollow fiber membranes. Typical example of hollow fiber blood processing devices includes dialyzer for
15   artificial kidney. The present invention is also preferably applied to artificial lung employing silicone rub-
ber hollow fiber membranes and to catheter made of silicone rubber.

    The present invention is more specifically described and explained by means of the following Exam-
ples. It is to be understood that the present invention is not limited to the Examples, and various change
and modifications may be made in the invention without departing from the spirit and scope thereof.
20

Example 1

    A dialyzer containing a bundle of 8,800 cellulose acetate hollow fibers each having an effective
length of 20 cm, an outer diameter of 230 μm and an inner diameter of 200 μm was placed in a gas-perme-
25   able sterile bag, both sides of which was made of a laminated polyester-polyethylene film and which had a
slit on the one side thereof with the slit portion being covered with a polyethylene non-woven fabric, and
the bag was sealed. The bag containing the dialyzer was sterilized by irradiation of gamma-rays in a dose
of 2.5 Mrad. The sterilized bag was inserted together with 10 g of Ageless as a deoxidizing agent into a
wrapping member in the form of bag and made from a laminated sheet consisting of a polyester film hav-
30   ing a thickness of 12 μm, an aluminum foil having a thickness of 9 μm and a polyethylene film having a
thickness of 40 μm, which layers were laminated in that order, and the wrapping member was heat-
sealed.

    The deodorizing effect was determined at appropriate time intervals. The results are shown in Table 1.
In Table 1, 1W, 2W and 4W represent the storage periods of 1, 2 and 4 weeks, respectively. The symbols
35   in Table 1 mean the followings:
O : No odor is detected.
X : Odor is detected.

Example 2
40
    The same procedures as in Example 1 were repeated except that a laminated sheet consisting of a poly-
ester film having a thickness of 12 μm, a polyethylene film having a thickness of 15 μm, an aluminum foil
having a thickness of 9 μm and a polyethylene film having a thickness of 40 μm, which layers were lami-
nated in that order, was used as a wrapping member.
45   The results are shown in Table 1.

Comparative Examples 1 and 2

    The same procedures as in Example 1 were repeated except that 50 g of an active carbon was used in-
50   stead of Ageless (Comparative Example 1) or both Ageless and the active carbon were not used
(Comparative Example 2).
    The results are shown in Table 1.

55

60

65

4

Table 1

Storage condition		Blank (no irradiation)	Irradiation (2.5 Mrad)			
Temp. (°C)	period		Ex. 1	Ex. 2	Com. Ex. 1	Com. Ex. 2
40	1 W	○	○	○	○	×
	2 W	○	○	○	○	×
	4 W	○	○	○	×	×
50	1 W	○	○	○	○	×
	2 W	○	○	○	×	×
	4 W	○	○	○	×	×
60	1 W	○	○	○	×	×
	2 W	○	○	○	×	×
	4 W	○	○	○	×	×

The results of Table 1 reveal that the use of a deoxidizing agent produces a noticeable deodorizing effect.

Example 3

The same hollow fiber as used in Example 1 was sterilized and packaged in the same manner as in Example 1. The aging of the strength of the follow fiber was determined. The results are shown in Table 2. In Table 2, each strength value is expressed in terms of an average value ± standard deviation for ten hollow fibers.

Comparative Example 3

The same procedures as in Example 3 were repeated except that no deoxidizing agent was used. The results are shown in Table 2.

Table 2

| Storage condition | | Blank (No irradiation) | | Irradiation (2.5 Mrad) | | | |
| | | | | Ex. 3 | | Com. Ex. 3 | |
Temp. (°C)	Period	Tensile strength at breaking (g/fiber)	Elongation at breaking (%)	Tensile strength at breaking (g/fiber)	Elongation at breaking (%)	Tensile strength at breaking (g/fiber)	Elongation at breaking (%)
40	1 W	76 ± 13	80 ± 11	76 ± 10	82 ± 13	75 ± 6	81 ± 12
	2 W	78 ± 10	81 ± 10	77 ± 8	79 ± 8	61 ± 8	73 ± 10
	4 W	77 ± 11	79 ± 12	77 ± 10	80 ± 10	55 ± 7	72 ± 14
50	1 W	78 ± 12	80 ± 10	77 ± 8	80 ± 12	70 ± 5	75 ± 8
	2 W	77 ± 11	79 ± 13	78 ± 6	81 ± 10	58 ± 7	72 ± 13
	4 W	79 ± 10	79 ± 7	76 ± 10	79 ± 12	49 ± 8	70 ± 10
60	1 W	78 ± 12	80 ± 10	76 ± 12	79 ± 9	58 ± 7	73 ± 8
	2 W	76 ± 10	80 ± 6	76 ± 8	80 ± 12	42 ± 5	67 ± 10
	4 W	77 ± 15	79 ± 11	75 ± 10	79 ± 8	31 ± 6	50 ± 12

The results of Table 2 reveal that the use of a deoxidizing agent contributes remarkably to prevention of decrease in strength due to aging from the hollow fiber.

Example 4

The same dialyzer as used in Example 1 was placed in the same sterile bag as used in the Example 1 and gamma-rays were irradiated thereto. The D value was determined with respect to Bacillus pumilus ATCC 27142. The results are shown in Table 3.

The same procedures as in the above were repeated with a dialyzer using polypropylene hollow fibers or an artificial lung using silicone rubber hollow fibers. The results are also shown in Table 3.

Comparative Example 4

The same procedures as in Example 4 were repeated except that each medical device was placed together with Ageless in the same oxygen-impermeable wrapping member as used in Example 1 and then subjected to irradiation of gamma-rays. The results are shown in Table 3.

Table 3

Hollow fiber	D value (Mrad)	
	Ex. 4	Com. Ex. 4
Cellulose acetate	0.213	0.405
Polypropylene	0.197	0.210
Silicone rubber	0.167	0.258

Results of Table 3 reveal that the irradiation of gamma-rays in the presence of a dioxidizing agent invites a great increase in the D value, particularly in the case of cellulose acetate hollow fiber. Therefore, it is desirable that the irradiation of gamma-rays is carried out in the absence of a dioxidizing agent.

In addition to the elements and ingredients used in the Examples, other elements and ingredients can be used in the Examples as set forth in the specification to obtain substantially the same results.

It will be apparent from the foregoing description that since the present invention comprises sealing a medical device contained in a gas-permeable sterile bag further in an oxygen-impermeable wrapping member together with a deoxidizing agent, it eliminates the oxygen from the wrapping member as well as from the sterile bag and even disposes of the oxygen emanating gradually from the medical device as well.

Furthermore, since the wrapping member is made of an oxygen-impermeable material, there is substantially no entry of external oxygen so that the deoxidizing agent may retain its function for an extended time period.

Claims

1. A radiation-sterilized medical device produced by the steps of:
placing a medical device (1) within a gas-permeable sterile bag (2);
sealing said gas-permeable sterile bag (2);
sterilizing said gas-permeable sterile bag (2) countaining said medical device (1) by gamma rays;
placing said sterilized gas-permeable bag (2) containing said medical device (1) and also placing a deoxidizing agent (3) within an oxygen-impermeable wrapping member (4); and
sealing said oxygen-impermeable wrapping member (4).

2. The medical device of Claim 1, wherein said radiation sterilization is a dry radiation-sterilization in a gaseous atmosphere.

3. The medical device of Claim 2, wherein said dry radiation-sterilization is sterilization with gamma rays.

4. The medical device of one of Claims 1 to 3, wherein said deoxidizing agent is based on activated iron oxide.

5. The medical device of one of Claims 1 to 4, wherein said medical device (1) is a hollow fiber blood processing device.

6. The medical device of Claim 5, wherein said hollow fiber blood processing device is a dialyzer using a cellulose acetate hollow fiber membrane.

7. The medical device of Claim 5, wherein said hollow fiber blood processing device is an artificial lung using a silicone rubber hollow fiber membrane.

8. The medical device of one of Claims 1 to 7, wherein said oxygen-impermeable wrapping member (4) is a laminated polyester-aluminum-polyethylene sheet.

9. The medical device of one of Claims 1 to 7, wherein said oxygen-impermeable wrapping member (4) is a laminated polyester-polyethylene-aluminum-polyethylene sheet.

Patentansprüche

1. Mittels Strahlung sterilisierter medizinischer Artikel, hergestellt durch die Schritte:
Einbringen eines medizinischen Artikels (1) in einen gasdurchlässigen sterilen Beutel (2);
Versiegeln des gasdurchlässigen sterilen Beutels (2);
Sterilisieren des den medizinischen Artikel (1) enthaltenden gasdurchlässigen sterilen Beutels (2) mit Gammastrahlung;
Einbringen des den medizinischen Artikel (1) enthaltenden sterilisierten gasdurchlässigen Beutels (2) und ebenso Einbringen eines Desoxidationsmittels (3) in ein sauerstoffundurchlässiges Verpackungselement (4); und Versiegeln des sauerstoffundurchlässigen Verpackungselements (4).

2. Medizinischer Artikel nach Anspruch 1, bei dem die Strahlungssterilisation eine trockene Strahlungssterilisation in einer Gasatmosphäre ist.

3. Medizinischer Artikel nach Anspruch 2, bei dem die trockene Strahlungssterilisation eine Sterilisation mittels Gammastrahlung ist.

4. Medizinischer Artikel nach einem der Ansprüche 1 bis 3, bei dem das Desoxidationsmittel auf aktiviertem Eisenoxid basiert.

5. Medizinischer Artikel nach einem der Ansprüche 1 bis 4, bei dem der medizinische Artikel (1) ein Hohlfaser-Blutverarbeitungsgerät ist.

6. Medizinischer Artikel nach Anspruch 5, bei dem das Hohlfaser-Blutverarbeitungsgerät ein Dialysegerät ist, bei dem eine Hohlfasermembran aus Celluloseacetat verwendet ist.

7. Medizinischer Artikel nach Anspruch 5, bei dem das Hohlfaser-Blutverarbeitungsgerät eine künstliche Lunge ist, bei der eine Hohlfasermembran aus Silicongummi verwendet ist.

8. Medizinischer Artikel nach einem der Ansprüche 1 bis 7, bei dem das sauerstoffundurchlässige Verpackungselement (4) ein laminierter Polyester-Aluminium-Polyäthylen-Bogen ist.

9. Medizinischer Artikel nach einem der Ansprüche 1 bis 7, bei dem das sauerstoffundurchlässige Verpackungselement (4) ein laminierter Polyester-Polyäthylen-Aluminium-Polyäthylen-Bogen ist.

Revendications

1. Article pour usage médical stérilisé par radiation, produit par les pas:
placer un article pour usage médical (1) dans un sachet (2) perméable aux gaz et stérilisé;
boucher ce sachet (2) perméable aux gaz et stérilisé;
stériliser ce sachet (2) perméable aux gaz et stérilisé contenant l'article pour usage médical (1) par rayons gamma;
placer ce sachet (2) perméable aux gaz et stérilisé contenant l'article pour usage médical (1) et aussi placer un agent de désoxydation (3) dans un emballage (4) imperméable à l'oxygène; et
boucher cet emballage (4) imperméable à l'oxygène.

2. Article pour usage médical selon la revendication 1, dans lequel cette stérilisation par radiation est une stérilisation sèche par radiation dans une atmosphère gazeuse.

3. Article pour usage médical selon la revendication 2, dans lequel cette stérilisation sèche par radiation est une stérilisation par rayons gamma.

4. Article pour usage médical selon l'une des revendications 1 à 3, dans lequel l'agent de désoxydation est à base d'oxyde ferrique activé.

5. Article pour usage médical selon l'une des revendications 1 à 4, dans lequel l'article pour usage médical (1) est un appareil à fibres creuses pour traiter le sang.

6. Article pour usage médical selon la revendication 5, dans lequel l'appareil à fibres creuses pour traiter le sang est un dialyseur utilisant une membrane à fibres creuses en acétate de cellulose.

7. Article pour usage médical selon la revendication 5, dans lequel l'appareil à fibres creuses pour traiter le sang est un poumon artificiel utilisant une membrane à fibres creuses en caoutchouc silicone.

8. Article pour usage médical selon l'une des revendications 1 à 7, dans lequel l'emballage (4) imperméable à l'oxygène est une feuille laminée en polyester-aluminium-polyéthylène.

9. Article pour usage médical selon l'une des revendications 1 à 7, dans lequel l'emballage (4) imperméable à l'oxygène est une feuille laminée en polyester-polyéthylène-aluminium-polyéthylène.

(12) EUROPÄISCHE PATENTSCHRIFT

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Beschreibung

Die Erfindung betrifft einen Kochextruder mit
einer Extruderschnecke zur Zuführung des Materi-
als für einen aus einem Nahrungsmittel bestehen-
den Hüllkörper, mit einem Düsenkopf, wobei durch
den Düsenkopf ein Füllrohr zur Zuführung von Füll-
material geführt ist und das Füllrohr von einem
Ringraum umgeben ist, der gegebenenfalls an eine
Unterdruckquelle anschließbar ist, wobei das Mate-
rial des Hüllkörpers unter einem Winkel zur Achse
des Füllrohrs zuführbar ist, und wobei das in Extru-
sionsrichtung aus dem Düsenkopf herausragende
Füllrohr lösbar innerhalb des Ringraumes angeord-
net und aus dem Düsenkopf herausziehbar ist.

Solche Kochextruder wurden bereits vorge-
schlagen (ältere europäische Patentanmeldung 0
173 982).

Bekannt sind in diesem Zusammenhang auch Dü-
senköpfe (europäische Patentanmeldung 0 071
183).

Extrudierte Nahrungsmittel, die als Gebäck
oder Snacks auf den Markt gebracht werden, er-
freuen sich immer größerer Beliebtheit. Insbeson-
dere extrudierte Nahrungsmittel aus mehreren Ma-
terialien, beispielsweise einem brotartigen Teig mit
Käsefüllung,werden gern gegessen. Schwierigkei-
ten bereitet oft die Dosierung der Füllung, da diese
aus Geschmacksgründen in nicht allzu großer Mas-
se vorliegen darf.

Der Erfindung liegt die Aufgabe zugrunde, ei-
nen Kochextruder derart auszugestalten, daß mit
ihm Beschichtungen von Hüllkörpern an deren In-
nenseite sehr leicht auszuführen sind.

Diese Aufgabe wird erfindungsgemäß dadurch
gelöst, daß am Austritts Ende des Füllrohres ein
Leitkegel mit zu dem Füllrohr gerichteter Spitze
angeordnet ist.

Mit dieser Ausbildung ist es möglich, daß die
unter Druck durch das Füllrohr geleitete Masse
über den Leitkegel nur an die Innenfläche des
mittels des Kochextruders extrudierten Hüllkörpers
gespritzt wird. Damit ist es möglich, ein rohrartiges
Gebilde zu schaffen, daß mit einer Schicht ge-
wünschter Stärke aus Käse, Schokolade oder dgl.
beschichtet ist.

Gemäß einer bevorzugten Ausführungsform ist
der Leitkegel über Haltestifte mit dem Stirnende
des Füllrohres verbunden.

Gemäß einer weiteren bevorzugten Ausfüh-
rungsform ist der Leitkegel in das Ende des Füll-
rohres eingesetzt und der Mantel des Füllrohres ist
im Endbereich mit einer Vielzahl von Durchgangs-
öffnungen oder Schlitzen ausgebildet.

In Weiterbildung der Erfindung ist in dem Füll-
rohr ein Füllrohr mit geringem Durchmesser ange-
ordnet. Damit ist es möglich, verschiedene Mate-
rialien in das Innere eines Hüllkörpers einzubringen

bzw. eine Beschichtung seiner Innenseite mit ver-
schiedenen Materialien vorzunehmen.

Unter anderem ist es denkbar, ein geeignetes Ma-
terial durch den Ringraum zwischen dem äußeren
und dem inneren Füllrohr zu leiten und durch das
innere Füllrohr ein Treibmittel, so daß nach dem
Aufspritzen des Materials auf die Innenfläche des
Hüllkörpers ein Aufschäumen dieses Materials er-
folgt.

Ein erfindungsgemäßes Verfahren zur Herstel-
lung einer Beschichtung der Innenfläche eines
Hüllkörpers ist dadurch gekennzeichnet, daß durch
das Füllrohr eine Beschichtungsmasse unter Druck
zugeführt wird und daß die Beschichtungsmasse
über den Leitkegel an die Innenfläche des Hüllkör-
pers geleitet wird.

Gemäß einer bevorzugten Ausführungsform
wird neben der Beschichtungsmasse ein Treibmit-
tel durch das Füllrohr und über den Leitkegel an
die Innenfläche des Hüllkörpers geleitet und durch
das Treibmittel wird die Beschichtungsmasse auf-
geschäumt.

Die Vermischung der Beschichtungsmasse mit
dem Treibmittel kann dabei unmittelbar vor dem
Leitkegel in dem Füllrohr erfolgen.

Es ist aber auch möglich, daß das Treibmittel
auf die Beschichtungsmasse nach deren Auftragen
auf die Innenfläche des Hüllkörpers geleitet wird,
indem beispielsweise das innere Füllrohr mit sei-
nem Ende über das Ende des äußeren Füllrohres
hervorsteht.

Als Treibmittel wird vorzugsweise CO_2 verwen-
det.

Ausführungsbeispiele der Erfindung werden
nachstehend anhand der Zeichnung näher erläu-
tert. Es zeigt:

Fig. 1   einen Längsschnitt durch einen Dü-
             senkopf,

Fig. 2   das Ende einer abgewandelten Aus-
             führungsform eines Füllrohres,

Fig. 3   das Ende eines Füllrohres zum Auftra-
             gen einer auftreibbaren Beschichtung,

Fig. 4   einen Querschnitt längs der Linie IV-
             IV von Fig. 3 und

Fig. 5   eine abgewandelte Ausführungsform
             eines Füllrohrendes.

Die in Fig. 1 gezeigte Anordnung zur Herstel-
lung eines Nahrungsmittels, bestehend aus einem
Hüllkörper und gegebenenfalls einer in diesem
Hüllkörper angeordneten Füllung, besteht aus einer
Düsenplatte 10, in welcher in einem Bereich ein
Düsenkopf 12 angeordnet ist. Die Düsenplatte 10
ist bei der gezeigten Ausführungsform aus drei
über Schrauben 14 zusammengespannte Platten
aufgebaut, wobei in einer hinteren Platte 16 ledig-
lich Durchgangsbohrungen für den Düsenkopf 12
und für die Einleitung des Materialstromes für den
Hüllkörper ausgebildet sind, eine mittlere Platte 18

ein Langloch aufweist, welches zur Führung des Materials für den Hüllkörper von dem Extruderende bis zu dem Düsenkopf dient, und eine vordere Platte 20, in welcher eine Durchgangsbohrung für den Düsenkopf und eine Durchgangsbohrung für eine Einstellschraube angeordnet ist, die anhand von Fig. 2 und 3 näher erläutert wird.

Der Düsenkopf 12 besteht aus einem Hohldorn oder Führungsrohr 22, welcher sich über eine angeformte Schulter 24 an der hinteren Platte 16 abstützt und über eine Mutter 26 an dieser Platte 16 festgelegt ist. In dem Hohldorn 22 ist eine rohrförmige Auskleidung 28 angeordnet, welche nach hinten über den Hohldorn 22 hinaus verlängert ist. In der vorderen Platte 20 ist eine Stauplatte 30 angeordnet, welche mit Durchgangsöffnungen 32 ausgebildet ist, durch welche das durch den Kanal 34 geführte Material für den Hüllkörper gepreßt wird. Dieses Material wird dann durch den Ringraum 36 geführt, der durch die Außenseite des Hohldorns 22 und die Innenseite eines Düseneinsatzes 38 gebildet wird. Der Düseneinsatz 38, der über eine Klemmplatte 40 an der Düsenplatte 10 befestigt ist, weist in der gezeigten Ausführungsform eine quadratische Öffnung auf. Das vordere Ende des Hohldornes 22 kann ebenfalls eine quadratische Außenkontur aufweisen, so daß ein Hüllkörper in Form eines Vierkantrohres ausgebildet wird.

Innerhalb des Hohldornes oder Führungsrohres 22 ist ein Füllrohr 42 vorgesehen, wobei zwischen der Innenseite der Auskleidung 28 und der Außenseite des Füllrohres 42 ein Ringraum 44 ausgebildet ist, welcher von einem T-förmigen Element 46 abgeschlossen ist. Dieses Element 46 ist über einen Stutzen 48 an eine Unterdruckquelle anschließbar, so daß der in dem rohrförmigen Hüllkörper während des Extrudierens gebildete Dampf abgesaugt werden kann. Dadurch wird ein Aufweichen des rohrförmigen porösen Hüllkörpers vermieden.

Das Füllrohr 42 ist durch das Element 46 hindurchgeführt, wobei über einen konischen Ring 50 und eine Mutter 52 eine Abdichtung des Elementes 46 an dem Füllrohr 42 erfolgt. Das Rohr 28 ist an dem Hohldorn 22 über eine mit einem Außengewinde versehene Muffe 54 festgelegt. Das Element 46 ist an dem Rohr 28 über einen konischen Dichtring 56 und eine Mutter 58 befestigt. Der konische Dichtring 50 liegt auf der Außenseite eines Rohrabschnittes 60 auf, durch welchen das Füllrohr 42 verschoben bzw. nach hinten aus dem Düsenkopf herausgezogen werden kann, Um ein Herausziehen aus dem Düsenkopf nach vorn zu verhindern, ist hinter dem Element 46 an dem Füllrohr 42 eine Klemme 62 vorgesehen, welche sich an dem Element bei gleichzeitigem Festhalten des Füllrohrs 42 abstützt.

Der vor den Düsenkopf ragende Bereich 64 des Füllrohres 42 ist zwischen zwei Formwalzen 66 und 68 hindurchgeführt. Die Formwalzen 66 und 68, die zur Ausbildung eines geeigneten Musters an der Außenseite des Hüllkörpers vorgesehen sind, können auch beispielsweise bis auf Rotglut aufheizbar sein, so daß an der Außenseite des Hüllkörpers eine lokale Wärmebehandlung erfolgen kann. Beispielsweise kann mit derartigen Formwalzen ein Warenzeichen in Form eines Brandzeichens aufgebracht werden. Während des Betriebs der Formwalzen dient der vordere Bereich 64 des Füllrohres 42 als Widerlager, so daß der Hüllkörper nicht unbegrenzt dem Druck der Formwalzen ausweichen kann. Wenn die Formwalzen mit sich ergänzenden Hohlkehlen ausgebildet sind, kann bei entsprechender Aufheizung ein Backen der Außenseite des Hüllkörpers erfolgen, so daß eine angebackene, knusprige Oberfläche des Hüllmaterials erreicht wird.

Vor dem Austrittsende des Füllrohres 42 ist ein Leitkegel 71 angeordnet. Der Leitkegel 71 ist dabei über Haltestifte 73 mit der Stirnfläche des Füllrohres 42 verbunden. Durch das Füllrohr wird beispielsweise ein Pulver oder eine Masse mit geeigneter Viskosität geführt. Wenn das Pulver oder diese Masse auf den Leitkegel 71 auftrifft, erfolgt eine Umlenkung, so daß das Pulver oder die Masse 75 an die Innenseite eines Hüllkörpers 77 gespritzt wird. Auf diese Weise erfolgt eine Beschichtung gewünschter Stärke an der Innenfläche des Hüllkörpers 77.

Fig. 2 zeigt ein Füllrohr 81, an dessen vorderem Ende ein Leitkegel 83 eingesetzt ist. Damit ein Pulver oder eine Masse, die durch das Füllrohr 81 geleitet werden, nach außen treten kann, ist das Füllrohr 81 mit einer Vielzahl von Durchgangsöffnungen 85 ausgebildet. Die Anzahl und Größe der Durchgangsöffnungen 85 muß dabei derart gewählt werden, daß keine Verstopfung des vorderen Endes erfolgt. Anstelle von Durchgangsöffnungen können auch Längsschlitze geeigneter Länge an dem Ende des Füllrohres 81 ausgebildet werden.

Fig. 3 zeigt ein Füllrohr 91, in welchem koaxial ein zweites Füllrohr 93 angeordnet ist. Das zweite Füllrohr 93 ist etwas kürzer als das Füllrohr 91. Mit Hilfe dieser Anordnung kann eine Beschichtung aus zwei Komponenten erfolgen, deren Vermischung vorzugsweise erst kurz vor dem Austritt aus dem Füllrohr durchgeführt werden soll. Beispielsweise ist es möglich, einen Hüllkörper 95 an der Innenseite mit einer Masse zu beschichten, welche auftreibt, so daß anstelle einer dünnen Schicht eine luftige Schicht größerer Stärke ausgebildet werden kann. Durch den von den Füllrohren 91 und 93 gebildeten Ringraum 97 kann beispielsweise eine schokoladenartige Masse geleitet werden, während durch das Füllrohr 93 ein Treibmittel wie beispiels-

weise CO_2 zugeführt werden kann. Wenn die Masse und das Treibmittel zu weit vor dem Austritt aus dem Füllrohr miteinander vermischt werden würden, würde wegen mechanischer Beanspruchung ein Zusammenfallen dieser aufgetriebenen Masse erfolgen, so daß die gewünschte Beschichtung nicht erreicht würde. Da die Vermischung der Beschichtungsmasse 98 mit dem Treibmittel 100 erst kurz vor dem Austritt aus dem Füllrohr erfolgt, kann die Konsistenz der Beschichtungsmasse erhalten werden.

Fig. 4 zeigt einen Querschnitt durch den Füllkörper 95. Im Inneren ist eine aufgetriebene Schicht 102 aus der Beschichtungsmasse 98 und aus dem Treibmittel 100 ausgebildet.

Fig. 5 zeigt eine abgewandelte Ausführungsform. Mit dieser Ausführungsform ist es möglich, das Treibmittel erst an die Beschichtungsmasse zuzuführen, wenn diese bereits als dünne Schicht an der Innenseite eines Hüllkörpers angeordnet ist. Dazu ist in einem Füllrohr 110 koaxial ein zweites Füllrohr 112 mit geringerem Durchmesser angeordnet. Vor dem Austrittsende des Füllrohres 110 ist ein Leitkonus 114 an der Außenseite des Füllrohres 112 befestigt. Durch den Ringraum, der zwischen der Außenseite des Füllrohres 112 und der Innenseite des Füllrohres 110 gebildet wird, wird eine Beschichtungsmasse 116 geführt, die über den Konus 114 an die Innenseite eines Hüllkörpers 118 geleitet wird. Da das Füllrohr 112 länger ist als das Füllrohr 110, gelangt durch das Füllrohr 112 geführtes Treibmittel 120 später als die Beschichtungsmasse 116 an die Innenfläche des Hüllkörpers 118. Um das Treibmittel 120 gleichmäßig an die Beschichtungsmasse 116 zu leiten, ist vor dem Austrittende des Füllrohres 112 ein Leitkegel 122 angeordnet, der über Haltestifte 124 mit dem Füllrohr 112 verbunden ist. Das Treibmittel 120 wird von dem Leitkegel 122 abgelenkt und auf die Schicht aus der Beschichtungsmasse 116 gebracht, so daß danach ein Aufschäumen der Beschichtungsmasse 116 erfolgen kann. Nach dem Aufschäumen ergibt sich ein Füllkörper 118 mit einer im Inneren aufgeschäumten Schicht aus Beschichtungsmasse 116 und Treibmittel 120 analog Fig. 4.

Patentansprüche

1. Kochextruder mit einer Extruderschnecke zur Zuführung des Materials für einen aus einem Nahrungsmittel bestehenden Hüllkörper, mit einem Düsenkopf (12), wobei durch den Düsenkopf (12) ein Füllrohr (42) zur Zuführung von Füllmaterial geführt ist und das Füllrohr von einem Ringraum (44) umgeben ist, der gegebenenfalls an eine Unterdruckquelle anschließbar ist, wobei das Material des Hüllkör-

pers unter einem Winkel zur Achse des Füllrohrs (42) zuführbar ist, und wobei das in Extrusionsrichtung aus dem Düsenkopf (12) herausragende Füllrohr (42) lösbar innerhalb des Ringraumes (44) angeordnet und aus dem Düsenkopf (12) herausziehbar ist, dadurch gekennzeichnet, daß am Austrittsende des Füllrohres (42) ein Leitkegel (71) mit zu dem Füllrohr (42) gerichteter Spitze angeordnet ist.

2. Kochextruder nach Anspruch 1, dadurch gekennzeichnet, daß der Leitkegel (70) über Haltestifte (72) mit dem Stirnende des Füllrohres (42) verbunden ist.

3. Kochextruder nach Anspruch 1, dadurch gekennzeichnet, daß der Leitkegel (82) in das Ende des Füllrohres (80) eingesetzt ist und daß der Mantel des Füllrohres (80) im Endbereich mit einer Vielzahl von Durchgangsöffnungen (84) oder Schlitzen ausgebildet ist.

4. Kochextruder nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß in dem Füllrohr (91, 110) ein Füllrohr mit geringerem Durchmesser (93, 112) angeordnet ist.

5. Verfahren zum Beschichten der Innenfläche eines Hüllkörpers mit einem Kochextruder nach einem oder mehreren der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß durch das Füllrohr eine Beschichtungsmasse unter Druck zugeführt wird, und daß die Beschichtungsmasse über den Leitkegel an die Innenfläche des Hüllkörpers geleitet wird.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß neben der Beschichtungsmasse ein Treibmittel durch das Füllrohr und über den Leitkegel an die Innenfläche des Hüllkörpers geleitet wird, und daß das Treibmittel die Beschichtungsmasse aufschäumt.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die Vermischung der Beschichtungsmasse mit dem Treibmittel vor dem Leitkegel in dem Füllrohr erfolgt.

8. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Treibmittel auf die Beschichtungsmasse nach deren Auftragen auf die Innenfläche des Hüllkörpers geleitet wird.

9. Verfahren nach einem der Ansprüche 6 bis 8, dadurch gekennzeichnet, daß das Treibmittel CO_2 ist.

Claims

1. Cooking extruder having an extruder screw for feeding the material for a casing body consisting of a foodstuff, with a die head (12), a filling pipe (42) for feeding filling material being guided through the die head (12) and the filling pipe being surrounded by an annular chamber (44) which can be connected if appropriate to a source of subatmospheric pressure, the material of the casing body being feedable at an angle to the axis of the filling pipe (42) and the filling pipe (42) which projects from the die head (12) in the direction of extrusion being arranged within the annular chamber (44) such that it can be detached and pulled out of the die head (12), characterised in that a guide cone (71) with its tip directed towards the filling pipe (42) is arranged at the outlet end of the filling pipe (42).

2. Cooking extruder according to Claim 1, characterised in that the guide cone (70) is connected via retaining pins (72) to the end face of the filling pipe (42).

3. Cooking extruder according to Claim 1, characterised in that the guide cone (82) is inserted into the end of the filling pipe (80) and in that the wall of the filling pipe (80) is designed with a multiplicity of passage openings (84) or slits in its end region.

4. Cooking extruder according to one of Claims 1 to 3, characterised in that a filling pipe with smaller diameter (93, 112) is arranged in the filling pipe (91, 110).

5. Method for coating the inner surface of a casing body using a cooking extruder according to one or more of Claims 1 to 4, characterised in that a coating material is fed under pressure through the filling pipe and in that the coating material is conducted via the guide cone to the inner surface of the casing body.

6. Process according to Claim 5, characterised in that, apart from the coating material, a blowing agent is conducted through the filling pipe and via the guide cone to the inner surface of the casing body and in that the blowing agent foams the coating material.

7. Process according to Claim 6, characterised in that the mixing of the coating material with the blowing agent takes place upstream of the guide cone in the filling pipe.

8. Process according to Claim 6, characterised in that the blowing agent is conducted to the coating material after the latter has been applied to the inner surface of the casing body.

9. Process according to one of Claims 6 to 8, characterised in that the blowing agent is CO_2.

Revendications

1. Cuiseur-extrudeur, avec une vis extrudeuse pour alimenter le matériau nécessaire pour un corps enveloppant en produit alimentaire, et avec une tête de filière (12), un tube de remplissage (42) pour alimenter du matériau de remplissage étant guidé à travers la tête de filière (12), et le tube de remplissage étant entouré d'un espace annulaire (44), qui peut éventuellement être raccordé à une source de dépression, le matériau du corps enveloppant pouvant être alimenté sous un angle par rapport à l'axe du tube de remplissage (42), et le tube de remplissage (42), qui dépasse hors de la tête de filière (12) dans la direction d'extrusion, étant disposé de manière amovible à l'intérieur de l'espace annulaire (44) et pouvant être sorti de la tête de filière (12) en le tirant, **caractérisé** en ce qu'un cône directeur (71), dont la pointe est dirigée vers le tube de remplissage (42), est disposé à l'extrémité de sortie du tube de remplissage (42).

2. Cuiseur-extrudeur selon la revendication 1, **caractérisé** en ce que le cône directeur (70) est assemblé par des axes de fixation (72) à l'extrémité frontale du tube de remplissage (42).

3. Cuiseur-extrudeur selon la revendication 1, **caractérisé** en ce que le cône directeur (82) est introduit dans l'extrémité du tube de remplissage (80) et en ce que l'enveloppe du tube de remplissage (80) est dotée, dans la région terminale, d'une pluralité d'ouvertures débouchantes (84) ou de fentes.

4. Cuiseur-extrudeur selon l'une quelconque des revendications 1 à 3, **caractérisé** en ce qu'un tube de remplissage de diamètre inférieur (93, 112) est disposé dans le tube de remplissage (91, 110).

5. Procédé pour enduire la face intérieure d'un corps enveloppant à l'aide d'un cuiseur-extrudeur selon l'une quelconque des revendications 1 à 4, **caractérisé** en ce qu'on alimente à travers le tube de remplissage une masse d'enduction sous pression, et en ce que la masse d'enduction est dirigée, par l'intermé-

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diaire du cône directeur, sur la face intérieure du corps enveloppant.

6. Procédé selon la revendication 5, **caractérisé** en ce qu'en plus de la masse d'enduction, on dirige un agent gonflant à travers le tube de remplissage et, par l'intermédiaire du cône directeur, sur la face intérieure du corps enveloppant, et en ce que l'agent gonflant fait gonfler la masse d'enduction.

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7. Procédé selon la revendication 6, **caractérisé** en ce que le mélange de la masse d'enduction avec l'agent gonflant s'effectue avant le cône directeur dans le tube de remplissage.

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8. Procédé selon la revendication 6, **caractérisé** en ce que l'agent gonflant est dirigé sur la masse d'enduction après avoir appliqué cette dernière sur la face intérieure du corps enveloppant.

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9. Procédé selon l'une quelconque des revendications 6 à 8, **caractérisé** en ce que l'agent gonflant est du CO_2.

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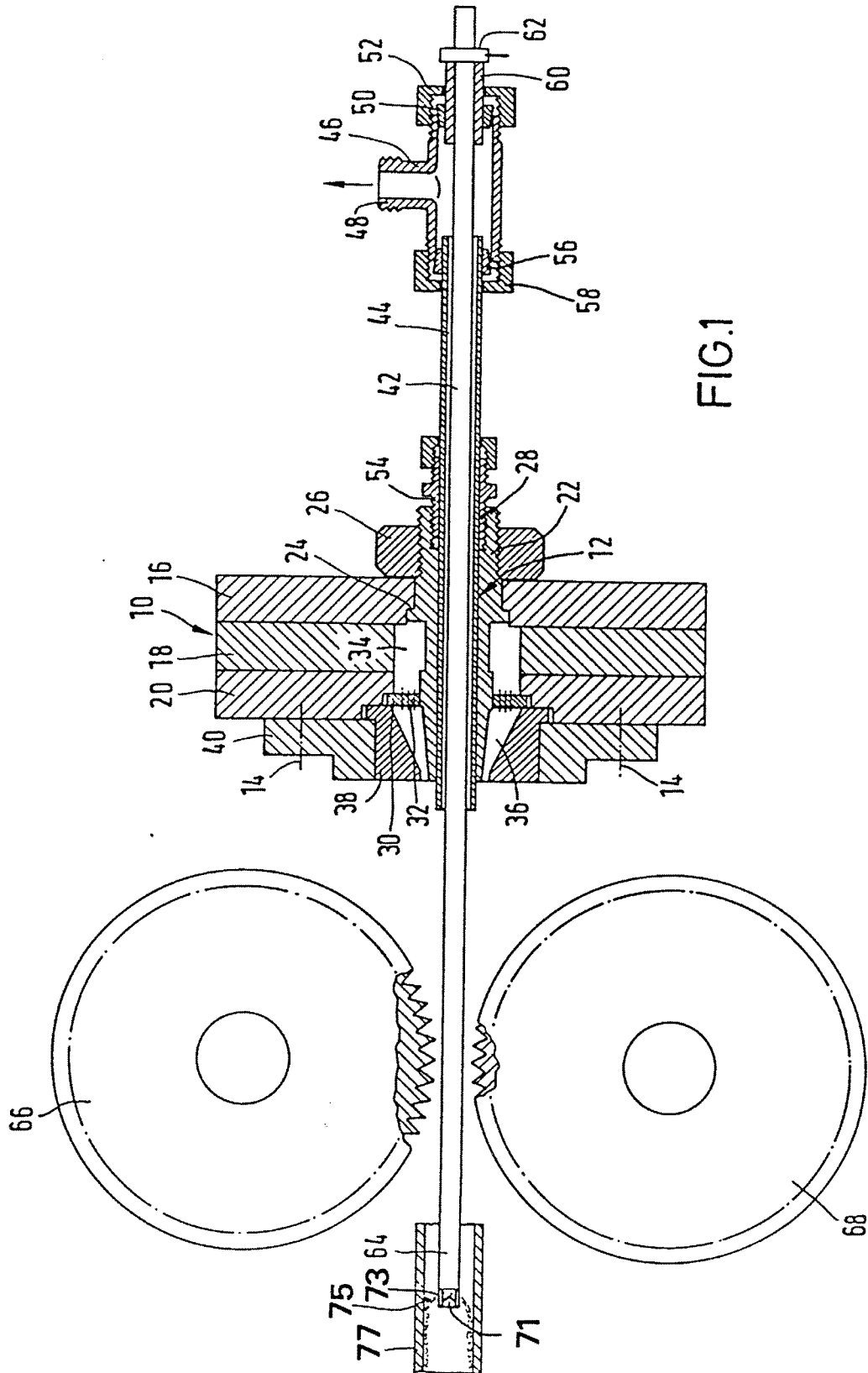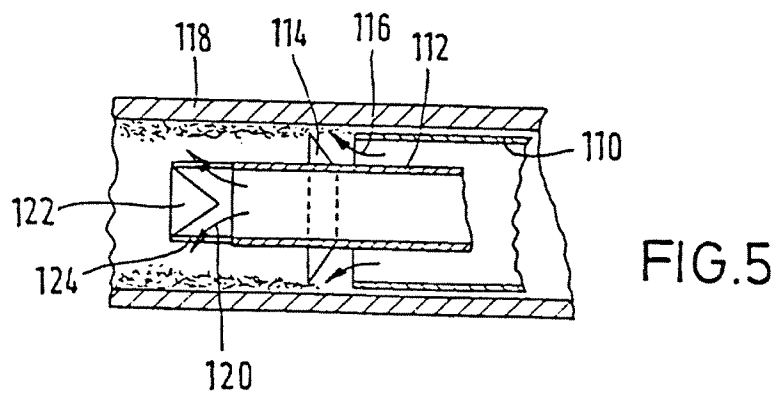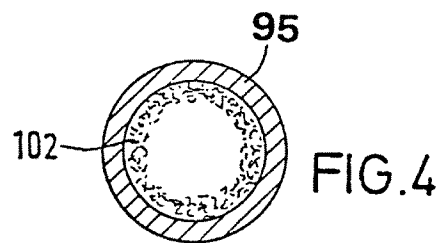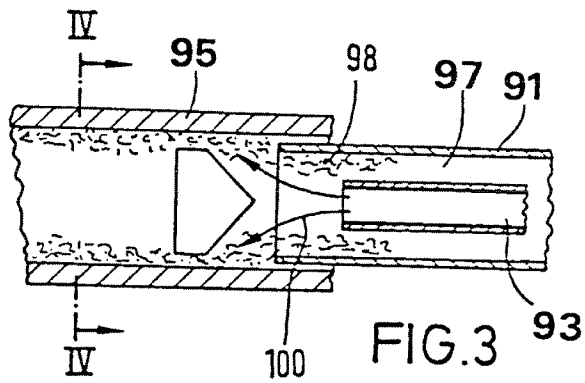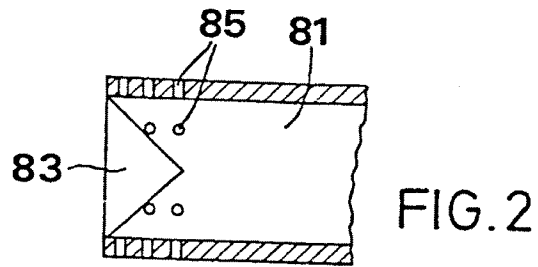
FIG.1

FIG.2

FIG.3

FIG.4

FIG.5

EUROPEAN PATENT SPECIFICATION

(54) **Ultrahigh molecular weight linear polyethylene, articles and processes of manufacture.**

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Description

BACKGROUND OF THE INVENTION

5   1. Field of the Invention

This invention relates to a novel ultrahigh molecular weight linear polyethylene (UHMWLPE). This novel UHMWLPE, in the form of a shaped article, exhibits in various embodiments a unique combination of properties making the material useful as a bearing surface, in general, but particularly useful as a prosthetic
10   hip joint cup and as other prosthetic shapes for replacement of other joints of the human body.

2. Description of the Prior Art

In U.S. Patent No. 3,944,536 (March 1976), Lupton et al describe UHMWPE in the form of a fabricated
15   article exhibiting an elastic modulus of 340,000 to 500,000 psi, a tensile impact strength of 140 to 600 ft lb/in^2, a density of 0.95 to 0.98 g/cc at 25°C, a crystalline melting point of 142 to 148°C (as measured by differential thermal analysis) and a unique crystalline form characterized by the absence of fold spacings of 50-2000 Angstrom units (Å) and the presence of crystal spacings of about 10,000 Å. The critical feature of the process of producing this UHMWPE is disclosed to involve inducing crystallization of the molten
20   polymer above 150°C by rapidly increasing the applied pressure from an initial level of 1 to 1000 atmospheres to a second level of 2000 to 7000 atmospheres and then cooling rapidly while maintaining a pressure sufficient to maintain the polyethylene in the solid phase until the temperature is below the crystalline melting point of the polyethylene at atmospheric pressure.
In Kunstuffe German Plastics 77 (1987) pp. 617-622, in an article entitled "Ultrahigh Molecular
25   Polyethylene for Replacement Joints", Eyrer et al. point out that the service life of joint replacements made of UHMWPE is limited. Analysis of the damage to over 250 explanted hip cups and tibial plateaus revealed a changed property profile which they explained by post-crystallization resulting from oxidative chain decomposition. They suggested optimizing the processing of polyethylene under higher pressure and higher temperature to increase the degree of crystallinity. The Eyrer et al. product displays a creep of
30   above 5% at a compression of 1000 psi (6.9 N/mm^2) for 24 hours at 37°C.
One of the most remarkable advances in the medical field in recent years is the development of prosthetic joints, particularly the load bearing hip. The crippled and sometimes bed ridden elderly can walk again. The key to this development is UHMWPE because, not only does it have the necessary impact strength, but it initiates no adverse blood reactions. But at present, these prosthetic joints are limited to the
35   older, less active segment of the population because the polymer tends to creep under the pressure that a younger more active person might develop while involved in recreation or employment. The creep would cause the loss of the close tolerance required between the plastic socket and the polished metal ball attached to the femur. These changes in dimensions disturb the distribution of walking forces which in turn accelerates more creep and wear. Eventually the increased pain requires a traumatic revision operation.
40   One objective of this invention is to provide UHMWPE prosthetic joints with improved creep resistance hence removing some of the age restriction existing on the present polyethylene joints.

SUMMARY OF THE INVENTION

45   The object of this invention is to provide a tough UHMWLPE composition and article with creep resistance that is less than 1% (as measured at a temperature of 23 ± 1°C and a relative humidity of 50 ± 2% for 24 hours under a comparison of 1000 psi) and that maintains excellent tensile and flexural properties.
Specifically, the product of this invention is a composition exhibiting an elastic or flexural modulus of
50   250,000-500,000 psi (1724 - 2488 MPa), a tensile stress at yield of 3500-4500 psi (24.1 - 31.0 MPa), a tensile stress at break of 4000-9000 psi (27.6 - 62.1 MPa), a tensile modulus 300,000-700,000 psi (1724 - 4827 MPa), preferably 300,000-600,000 psi (2069 - 4137 MPa), an elongation of 200-500%, a notched Izod impact resistance of 12-25 ft. lb. per in. (641 - 1335 Nm/m) of notch, a creep at a compression of 1000 psi (6.9 MPa) of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the
55   polyethylene having a molecular weight of 1,000,000-10,000,000 (the molecular chain length between folds being greater than 3500Å), a single crystalline melting point of greater than 144°C (as measured by differential scanning calorimetry) the reduction in said melting point upon reheating being greater than 11°C above that of the starting polymer and an infrared crystallinity index of at least about 0.45, preferably at

least 0.5. The composition may be formed into an article.

The process for obtaining the article of this invention involves six (6) important steps:

1. forming, by milling or casting or the like the article from UHMWLPE having a molecular weight of 400,000-10,000,000, preferably at least 1,000,000 and most preferably at least 6,000,000;

2. placing the article in a pressure vessel (e.g. an autoclave) substantially filled with a fluid that is inert to the article, preferably water;

3. heating the vessel to a temperature of at least 190°C, preferably 200°C-230°C, and raising the pressure in the vessel, usually by adding additional water, to at least 2800 atmospheres (ATM) (280 MPa), preferably at least 3000 ATM (300 MPa);

Alternatively, the article, water, and reactor are heated to about 200-230°C, the pressure is applied and the system held at this temperature while polymer slowly loses heat of crystallization and solidifies.

Also, the pressure can be applied at any temperature during the heating cycle if the temperature exceeds about 200°C.

4. maintaining the temperature and pressure substantially as selected in step 3 for at least 0.5 hour, preferably at least one hour;

5. thereafter, cooling by reducing the temperature to a temperature at least below about 160°C-170°C preferably to 160°C or below, most preferably below 140°C, while maintaining a pressure of at least 2800 ATM (280 MPa) preferably at least 3000 ATM (300 MPa) at a slow rate, the rate of cooling being such that temperature gradients in the shaped article are substantially avoided. The polymer must be cooled slowly at the high pressure until it is fully crystallized. At 3000 ATM (300 MPa) pressure, the crystallization temperature of UHMWLPE of over one million molecular weight is in the range of 170°C-190°C. The pressurized vessel should be cooled slowly to insure that the temperature of the polymer is not significantly above the vessel temperature, particularly if the pressure vessel construction does not permit means for measuring the temperature of the polymer itself.

6. cooling and releasing the pressure on the shaped article in a manner such that any remelting of the article is prevented. This is accomplished by cooling at least to a temperature below the atmospheric pressure melting point, i.e., about 130°C-135°C preferably below 120°C, most preferably below 100°C and releasing the pressure to reduce it from at least 2800 ATM (280 MPa) to approximately 1 ATM (0.1 MPa), either sequentially or simultaneously. It should be understood that it is necessary to cool the polymer to a temperature below its melting point at any particular pressure to ensure that none of the polymer melts as the pressure is reduced since lowering the pressure lowers the melting point.

As an optional seventh step, it is advisable to shave the surface of the article, i.e. remove approximately the outer 2 millimeters that might contain any fluid-affected polymer.

A very important step is the fifth step, i.e. cooling in a manner that limits severe temperature gradients in the article. For example, for a 1 inch X 6 inch rod (25mm x 150mm), a cooling rate of approximately 10°C per hour is usually necessary. Although cooling rates no greater than 10°C per hour are preferred, cooling rates as high as about 35°C per hour have been used to provide the product of this invention. However, these latter rates require careful control in order to limit temperature gradients during cooling. Cooling rapidly, as taught in the prior art, will not provide the article of this invention. This invention is particularly useful for manufacturing shaped articles where temperature gradients pose a problem during the cooling step, i.e., where the article's cross-sectional dimensions are at least 1 inch x at least 1 inch (25mm x 25mm), usually for joints at least 1 inch x at least 2 inches (25mm x 51mm) Specifically, the importance of this step and of this invention is manifest in producing articles having as its smallest dimension 0.2 inch (5mm), i.e., at least 0.2 inch (5mm) in thickness. It has been found that in such articles, the temperature gradients must still be controlled by the process of this invention in order to obtain the product of this invention.

Alternatively, for steps 2 and 3, the pressure vessel can be used more efficiently by preheating polymer outside the reactor because heating polyethylene is a very slow process due to its high heat of fusion and its thermal insulation property. It can be heated in an oven, preferably in an inert atmosphere to prevent oxidation, particularly when the tempereature is above 160°C. Because the UHMW polyethylenes do not flow when melted, they can be handled while hot and transferred to the preheated pressure vessel without deforming.

Product resulting from this modified process also is excellent for orthopedic replacement and has certain superior characteristics. Values demonstrating these superior, enhanced qualities are shown in Example 11.

In addition to utility in the field of orthopedic replacement, the products prove useful in other applications also requiring the special properties of the products. Not only shaped articles are of interest, but also films and fibers as well as other "downstream" forms and unshaped granular forms of the product

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will prove useful. Film formed of the product of Example 5 is exemplified in Example 13. These examples are illustrative only, and other forms, shaped and unshaped, of the composition are contemplated within the scope of the invention. Therefore, "article" shall include both shaped articles and unshaped articles.

In a process more recently developed for manufacturing the product of this invention, the fluid used in the pressure vessel could be a gas that does not affect the UHMWLPE adversely. Specifically, the shaped article is formed from commercially available UHMWLPE. In the second step, the article is placed in a pressure vessel containing the fluid, in this case argon. However, it is necessary in the case where argon is used, to protect the UHMWLPE from any entry of the gas into the polymer by surrounding the article with a thin stainless steel or similar metal can as described in copending U.S. Patent Application (DE-0289C) filed to S. Li on November   , 1989 which is a continuation-in-part of U.S. Serial No. 07/426,918 filed on October 24, 1989 which in turn is a continuation-in-part of U.S. Serial No. 07/288,576 filed December 22, 1988 which in turn is a continuation-in-part of U.S. Serial No. 07/278,912 filed on December 2, 1988. It should be understood that other gaseous fluids may be used in place of argon. So long as the gas does not adversely affect or is prevented from adversely affecting the polymer and is not affected by the temperatures and pressures used in the process, the gas may be used.

In the next step, a pressure of at least 2800 ATM is applied and the vessel is heated to about 220°C for about 6 hours. Thereafter, the temperature is "ramped" down at a rate no greater than about 10°C per hour to about 160°C while maintaining the pressure above 2800 ATM (280 MPa). The temperature is then "ramped" down at a maximum rate to 50°C while maintaining the high pressure, after which the pressure is released.

A further embodiment of the invention involves the following important steps:

1. forming by milling a casting or the like, the article from UHMWPE having a molecular weight of 400,000-10,000,000, preferably at least 1,000,000;

2. subjecting said article to a temperature of 190-340°C, preferably 320-340°C, for at least 0.5 hour, preferably at least one hour, in an inert atmosphere; and

3. cooling the article non-precipitously to a temperature of about 130°C or below. As in the other embodiments, the rate of cooling is such that temperature gradients in the shaped article are substantially avoided. Again, the rapid cooling sought in the prior art will not provide the article of this embodiment. The product of this non-pressurized embodiment is particularly useful for manufacturing shaped articles where temperature gradients pose a problem during the cooling step, i.e., where the article's cross-sectional dimensions are at least 1 inch x at least 1 inch (25mm x 25mm), usually for joints at least 1 inch x at least 2 inches (25mm x 51mm). Specifically, the importance of this step and of this invention is manifest in producing articles having as its smallest dimension 0.2 inch (5mm), i.e., at least 0.2 inch (5mm) in thickness.

For purposes of this invention, ultrahigh molecular weight linear polyethylene (UHMWLPE) is defined as a linear polyethylene having an estimated weight-average molecular weight in excess of about 400,000, usually 1,000,000 to 10,000,000 as defined by a melt index (ASTMD-1238) of essentially zero and a reduced specific viscosity (RSV) greater than 8, preferably 25-30. The relationships of RSV to intrinsic viscosity and to molecular weight are those developed by R. Chaing as presented by P. S. Francis et al. in J. Polymer Science, 31, 453 (1958).

It is envisioned that the modifications of adding a preliminary step heating the product to 320-340°C will also provide superior characteristics to the product described by Li.

The improved properties of the products of this invention in its various embodiments are reflected in a tensile modulus of at least 300 kpsi (2069 MPa), a flex modulus of at least 250 kpsi (1724 MPa), ultimate tensile strength greater than 4000 psi (27.6 MPa), yield strength greater than 3500 psi (24.1 MPa) and an elongation at break no greater than 500%.

A very important property of the product of this invention is its creep resistance. For prosthetic devices, e.g. knee, hip, elbow joints, etc., any substantial creep can be devastating in the loss of the benefits of extremely expensive surgery. Thus, the shaped articles of this invention display as little as a 0.5% loss in thickness when subjected to a compression pressure of 1000 psi (6.9 MPa) for 24 hours at a temperature of 23°C and a relative humidity of 50% in accordance with ASTM D-621.

For some applications, still lower creep, higher stiffness, higher elongation, and particularly higher tensile strengths at yield are necessary. These can be introduced by the enhancing process if the polyethylene is first thermally heated at 320-340°C for thirty minutes or longer. The process depends on heating the polymer as near as possible to, without reaching, its decomposition point. The hot polymer should be cooled slowly because very rapid cooling, such as immersion in cold water, causes internal voids to form. This is caused by the combination of large volume changes polyethylene undergoes when melting (about 30%) and its poor heat conductivity. A convenient method is to allow the polymer to cool wrapped in

insulation. The hot polyethylene can be put directly into the hot pressure vessel or it can be cooled and reheated to the normal 200°C in the pressure vessel.

The improved properties of the product of this part of the invention are reflected in tensile modulus of at least 350 kpsi (2413 MPa), a tensile strength at yield of 3500-5400 psi (24.1 - 37.2 MPa), and a creep value
5   of less than 0.6%.

In addition, the thermally heated polymer, still in the folded chain form used to make this superior form of this invention, in itself has improved elongation, crystallinity, and impact resistance over the starting material, but it is not equivalent to the enhanced form of polyethylene.

Perhaps the most characteristic property of the product of this invention is its infrared crystallinity index
10   (IRCI). This property, which provides a reasonably accurate reflection of the crystallinity of this material, is in a range never before attained with any UHMW polyethylene materials. To determine this index, samples are first obtained by microforming thin sections. Heat and pressure should be avoided during preparation of the samples. ICRI is the ratio of the band at 1894 reciprocal centimeters (cm^{-1}) to the band at 1305 reciprocal centimeters (cm^{-1}). Since the band at 1894 cm^{-1} is attributed to the crystalline nature of the
15   material and the band at 1305 cm^{-1} is attributed to its amorphous nature, ICRI increases as the crystallinity increases. The product of this invention displays an IRCI of at least about 0.45. In fact, values of 0.73 and higher have been obtained. On the other hand, IRCI values for prior known UHMWLPE's seldom reach above 0.3.

The invention will be more clearly understood by referring to the drawings and examples, which follow.
20   In the drawings, Figure 1 is a schematic diagram of the equipment used in the process for forming the product of the invention using argon gas; and Figure 2 is a schematic diagram of the equipment used in the hydrostatic process.

In the examples, most of the properties are measured using standard ASTM tests.

All of the physical measurements were carried out under constant humidity (50% relative humidity) and
25   temperature (23°C) conditions.

Tensile modulus, ultimate tensile strength, yield strength and elongation were measured according to ASTM D-638 with the following modifications:
- samples machined into shape without lubricating fluid
- type I tensile bar
30   - cross head speed = 0.2"/min (5mm/min) for tensile modulus
        2.0"/min (51mm/min) for tensile stress and elongation.

Creep resistance was measured in accordance with ASTM D-621 with the following modifications:
- samples machined into cylinders or cubes without the use of lubricating fluids
- samples measured 0.5" x 0.5" x 0.5" (13 x 13 x 13mm)
35   Flexural properties were measured according to ASTM D-790 with the following modifications:
- samples machined into shape without the use of lubricating fluids
- typical flex bar measures 0.125" thick x 0.5" width x 5" length (3 x 13 x 127mm)
- span or gauge is 2.0" (51mm). (This was determined by a span/depth ratio of 16/1.)
- cross head speed = 0.05"/min (1mm/min) (calculated based on span).
40   Impact resistance was measured using the notched Izod test given in ASTM D-256 with the following modifications:
- samples machined into shape without the use of lubricating fluid
- type A or notched IZOD
- specimen size is 0.5" x 2.5" (13 x 64mm)
45   - 0.4" from bottom of vertex to opposite side
- 1.25" (32mm) impacted end (from end of bar to vertex of notch)
- the notch should be the specified angle of 22.5 degrees.

It should be appreciated that in all embodiments of the invention the step of forming the article by milling, casting, or the like from UHMWLPE may be performed as the first step in the process (i.e., before
50   heating or preheating) or as the last step in the process (i.e., after the cooling step).

The following non-limiting examples, including the improved and superior embodiments, illustrate the basic principles and unique advantages of the present invention. Various changes and modifications may be made without departing from the spirit and scope of the present invention.

55   EXAMPLE 1

The material used in this example is American Hoechst Hostalen 415 GUR ultrahigh molecular weight polyethylene. It was obtained in the form of bars, 3" in diameter and up to 5' long in length (76mm to

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1.5m). The material will be referred to as UHMWLPE. The molecular weight was over 1,000,000.

One or more pieces of the UHMWLPE 11 were placed into stainless steel, seamless, 48" (1.22 m) long cylinders or sleeves 12. The thickness of the stainless steel was 1/8" (3mm). The bottom of the cylinders was closed by welding a stainless steel cap 13 onto the bottom of the cylinder. The top of the cylinder was

5   partially closed by welding on a modified cap 14 which contained a vacuum port 15. The cylinder was then evacuated using a vacuum pump and sealed by crimping the port to form a can that surrounds the piece of UHMWLPE completely. The sealed cylinder was then placed in a containment vessel 16 large enough to hold 15 cylinders. The containment vessel 16 was then placed into a hot isostatic pressing (HIP) unit 17 with molybdenum heating units 18. Thermocouples were added to monitor the temperature of the cylinders.

10   The basic function of the HIP process is to uniformly heat a load while applying pressure uniformly to all surfaces. The pressure medium used in this case was argon. The UHMWPE is protected from contact with the argon by the stainless steel cans.

The process conditions were:

1. Apply pressure to 39,000 psi. (269.1 MPa)

15   2. Heat to 220°C.

3. Hold for 6 hours at 220°C and a minimum pressure of 41,000 psi (282.9 MPa) (27 atmos.) (2.7 MPa).

4. Ramp temperature down at a rate no faster than 10°C per hour to 160°C. Pressure is maintained above 41,000 psi (282.9 MPa) during this time.

5. Ramp temperature down at maximum rate to 50°C while maintaining the pressure above 41,000 psi

20   (282.9 MPa)

6. Below 50°C, pressure may be let down and the cycle ended.

The UHMWPE rods were then removed from the sleeves and parts were fabricated for physical testing. It is noted that the material produced exhibits much higher tensile modulus, flex modulus, melting point, density and creep resistance than the starting material (Control A).

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Material	DSC Melting Point (°C)	Density (grams/cc)	IRCI
Control	137.0–140.7°C	.93–.94	0.24
Example 1	148.0–152.0°C	.947	≳ 0.45

ASTM D638	Control A	Example 1
Flex Modulus kpsi (MPa)	165 (1138)	291 (2006)
Tensile Modulus kpsi (MPa)	185 (1276)	315 (2172)
Ultimate Tensile kpsi (MPa)	4500 (31028)	4688 (32324)

ASTM D638

Yield kpsi (MPa)	3476 (23967)	4082 (28145)
Elongation (break) %	262	227

[values are averages of 5 tests]

ASTM D621 Creep Test

Load

500 psi (3.45 MPa)	.5	.3 % deformation
1000 psi (6.9 MPa)	1.6	.7
2000 psi (13.8 MPa)	5.9	2.4

Additional evidence of the products' distinctiveness is found in data produced by small angle X-ray testing. A truly characteristic small-angle X-ray scattering plot of desmeared intensity (by the method of P. W. Schmidt, Acta Cryst., 13, 480 (1960) and Acta Cryst., 19, 938 (1965)) (I x (2 theta) squared) versus scattering angle (2 theta) for the material of the invention exhibits two distinct scattering peaks associated with crystal long-spacings in the range of 480 angstroms (at 2 theta = .184 degrees) and 4610 angstroms (at 2 theta = .0192 degrees). The presence of the sharp diffraction peak at the lower angle is indicative of an extended polymer chain conformation (with a lamellar thickness greater than 2000 angstroms) whereas the more diffuse higher-angle peak corresponds to a lamellar thickness characteristic of conventional folded chain PE. This provides clear evidence for the presence of two scattering peaks in the subject invention material which correspond to lamellar thicknesses both above and below 2000 angstroms. By comparison, the previously patented extended chain polyethylene of Lupton et al., was reported to exhibit a complete absence of any detectable small angle X-ray scattering in the range of 50 to 2000 angstroms. Consequently this work demonstrates that the subject invention material is morphologically distinguishable from Lupton et al.

EXAMPLE 2

The material used in this example is an ultrahigh molecular weight polyethylene obtained from Jet Plastics, Inc.

A rod 21 measuring 6" x 1 1/8" (152 x 32mm) was placed in the cavity 22 of a stainless steel, seamless, cylindrical reactor 23. The cavity 22 had a diameter of 1.35" (34mm) and was about 9" (23mm) long.

Water was fed into the cavity 22 at the entry port 24 through the use of a high pressure water pump 25 powered by compressed air. Simultaneously, the reactor was heated by electrical heaters 26 surrounding the reactor.

In the first step, the rod 21 was heated to a temperature of 220°C under a hydrostatic pressure of 2000 ATM (200 MPa). The pressure was raised to 3000 ATM (300 MPa) while the temperature was maintained at 220°C for 2 hours. The temperature was permitted to fall to 209°C over another 2 hour period, and then to about 182°C in 4 hours. Finally, the rod was cooled to 49°C by subjecting the reactor 23 to compressed air from the blower 27 over a period of one hour and the pressure released.

The rod was removed from the reactor and the surface was shaved. The product, a sample taken substantially from the center of the rod, displayed a DSC melting point of 154.5°C, and, on reheating, a DSC melting point of 140°C.

The material, when subjected to a compression pressure of 1000 psi (6.9 MPa) for 24 hours at a temperature of 23°C and a relative humidity of 50% in accordance with ASTM D-621, deformed only 0.4%.

The other properties of the product were:

flexural modulus	- over 250 kpsi (1724 MPa)
tensile modulus	- over 300 kpsi (2068 MPa)
tensile stress (yield)	- over 3500 psi (24.1 MPa)
tensile stress (break)	- over 4000 psi (27.6 MPa)
elongation (break)	- less than 500%.

Its infrared crystallinity index was over 0.5.

The hydrostatic process described in Example 2 is the best mode for preparing the product of this invention. This process has important advantages. The pressure transfer liquid, water, is non-toxic and inexpensive. The hydraulic pressure is applied equally in all directions resulting in a substantially homogeneous product. This compares to processes shown in the prior art where hydraulic pressure is applied by a piston or a ram. In these latter cases, the high shrinkage polymer tends to solidify along the heat-escaping walls making it difficult for the pistons to advance and still apply the pressure uniformly. The result is a heterogeneous product.

It should be understood that although water is the preferred liquid fluid to use in the process, other liquids, with the same criteria as mentioned for gases, are also useful. Thus, methanol, ethanol, glycerin, glycols, etc. in addition to various aqueous solutions may be used.

The salt selected for an aqueous solution may be one that imparts a desirable property to the surface of the shaped article.

EXAMPLE 3

This experiment was carried out in a manner similar to Example 2 except that the pressure in the first step was 3000 ATM (300 MPa). The material was maintained at 220°C under 3000 ATM (300 MPa) for 4 hours. The temperature was allowed to fall to 190°C over an 8-hour period. After which, it was cooled to 100°C in 1 hour.

Samples were taken from 1/8" (3mm) inside both ends of the rod and had melting points of 150.8°C and 153.2°C. When reheated, the melting points were 135.5°C and 138°C, respectively.

The infrared crystallinity index was 0.791; and the creep, when measured in accordance with ASTM D-621, was less than 1%. These measurements were obtained on a sample taken from the center of the rod.

EXAMPLE 4

The experiment was also carried out in a manner similar to Example 2 except for the following changes in the heating/cooling cycle:

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Heat at 211°C and 3000 ATM (300 MPa) and maintain for 1 hour;
Cool to 200°C in 1 hour at 3000 ATM (300 MPa);
Cool to 180°C over 5 hours at 3000 ATM (300 MPa) (cooling rate 200→180°C, 4°/hour); and
Cool to 33°C in 1 hour and 3 minutes.

The product from inside both ends melted at 150°C and on reheating, at 135.5°C. The product, when tested in accordance with ASTM D-621 displayed a creep of less than 1%. Its infrared crystallinity index was 0.652.

EXAMPLE 5

A reactor with the general configuration shown in Figure 2 having an internal diameter of 4" (102mm) and being 22" long (559mm), was charged with a 3 1/8" x 18 1/16" (79 x 459mm) rod of UHMWPE (made from polymer from American Hoechst, Hostalen GUR 415). The closed vessel was evacuated, filled with water, and heated to 232°C at which point the pressure was increased to 3000 ATM with the water pump. This pressure was maintained until the end of the experiment. The reactor was held between 210 and 230°C for 3 hours, cooled over 1 hour to 200°C, cooled to 175°C in 5 hours (5°/hour) and then cooled to 80°C in 7 1/2 hours.

The resulting product rod was still in a cylindrical form with very little warpage. It measured 3 1/8" x 17 15/16" (79 x 456mm). End pieces, 1/2" (13mm) thick, were cut off each end of the rod revealing a uniform white color. Samples taken from the center of the rod on these cuts gave melting points of 152.9°C (201 J/g) and 152.1°C (207 J/g) when heated at 20°C/minute. When reheated, the melting points were 137.5°C.

A six inch (152mm) section of the rod was sawed into 3/16" (5mm) thick shapes for physical tests, then carefully milled to remove saw marks to 1/8" (3mm) thickness. The resulting polymer had the following properties:

IZOD	18.7 ft. lb./in. of notch (998 Nm/m)
Flexural Modulus	298.9 kpsi (2061 MPa)
Tensile Properties	
Stress at yield	4190 psi (28.9 MPa)
Stress (max.) (at break)	5430 psi (37.4 MPa)
Elongation (at break)	280%
Modulus	378.3 kpsi (2608 MPa)
Creep Test, 1000 psi	0.6%

All tests at room temperature.
The crystallinity index (IRCI) was 0.528.

EXAMPLE 6

In this example, the product was prepared with an exceedingly smooth surface.

A polished brass disk, about 1 1/2" (38mm) diameter, 1/4" (6mm) thick was pressed at 160°C against a UHMW polyethylene plug. The combination was cooled under pressure and sealed in a heat shrinkable Teflon FEP™ tube. The polyethylene was converted in a hydrostatic system by this procedure in the vessel used in Example 5.

The heating, cooling cycle was as follows:
3000 ATM and 210°C in 1 hour;
3000 ATM 210°C to 200°C in 1 hour;
3000 ATM 200°C to 178°C in 6 hours, 45 minutes; and
3000 ATM 178°C to 23°C in 2 hours, 20 minutes.
(3000 ATM = 300 MPa)

The polyethylene did shrink so that it had a smaller diameter than the disk, but the polymer stuck to the surface. When forced apart, the surface was extremely smooth.

This technique is important in preparing complicated surfaces where smoothness is extremely important, such as on bearing surfaces such as medical prosthesis for knee and hip joints, or bearings for motor shafts, etc. Machine cutting polymers always leaves very small ridges.

EXAMPLE 7

The reactor of Figure 2, internal diameter 4" by 22" long was charged with a 3" x 18" (76mm x 457mm) rod of American Hoescht, Hostalen GUR 415 ultrahigh molecular weight polyethylene, water, and a
5   nominal pressure of 100 psi (7 MPa). The system was heated to 170°C to 176°C and held there for 1 hour, then the pressure was raised to 3000 ATM (300 MPa). The temperature was maintained at 179°C-174°C for 3 hours, during which time the polyethylene crystallized. The reactor was cooled to 79°C in 1.7 hours.
    Two samples were taken; one from the center of the rod and another 1/2 inch (13mm) from the outer surface of the rod. The melting points, as measured by DSC, were 150.9°C and 150.4°C, respectively, and
10 upon reheating, 136.6°C and 137/3°C. Thus, the increases in melting points were 14.3°C and 12.7°C, respectively. The infrared crystallinity index was 0.5.

EXAMPLE 8

15 This example shows that the polymer can be cooled at a rate as high as 34.5°C per hour in the critical cooling step (step 5) if proper precautions are taken to limit temperature gradients.
    A one inch rod of UHMWLPE from Jet Plastics, Inc. was used. It was placed in the pressure vessel with water and subjected to the following treatments:
    3000 ATM and 220°C for 2 hours;
20 3000 ATM, cool to 200°C in 50 minutes;
    3000 ATM, cool to 177°C in 40 minutes;
    3000 ATM, cool to 35°C in one hour.
    (3000 ATM = 300 MPa)
    A test sample taken one-half inch from the end of the rod and in the center displayed a DSC melting
25 point of 153.8°C, and, on reheating a DSC melting point of 139.7°C.
    The material, when subjected to a compression pressure of 1000 psi (6.9 MPa) for 24 hours at 23°C and a relative humidity of 50% in accordance with ASTM D-621 deformed 0.5%.

EXAMPLE 9

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Superior Enhanced UHMW Polyethylene prepared by Preheating Polymer to 325°C.

    A 3-1/16" x 15" (78 x 381mm) rod of UHMW polyethylene (Hoechst GUR415, fabricated by PolyHi) was heated to 325°C in an atmosphere of N₂ for six hours. The hot rod was quickly placed in a pressure vessel
35 preheated to 212°C. The vessel was sealed immediately and pressured with water to 3000 ATM. The cooling schedule was as follows:
    212° to 191°C 65 minutes
    191° to 181°C 63 minutes
    181° to 175°C 2 hours
40 175° to 174°C 6 hours, 26 minutes
    174° to 45°C 3 hours, 15 minutes
    The rod was cut into test samples and analyzed with the following results:

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DSC (Differential Scanning Calorimetry)

	Center of Bar	1 cm from Bar Edge
m.p., °C		
1st heat	150.5	152.4
2nd heat	137.9	139.0
ΔT	12.6	13.4
Heat of Fusion		
1st heat	198.8 J/g	
2nd heat	134.4 J/g	

Infrared Crystallinity Index

(Samples cut from within 5 mm of bar edge)

In Bar Direction	0.613
Perpendicular to Bar Direction	0.633

Flex Modulus (KPSI)

	424.0	(2923 MPa)
	386.1	(2662 MPa)

Deformation (Creep) ASTM D621 (% at 1000 psi
(6.9 MPa) load)

In Bar Direction   0.4

Perpendicular to Bar Direction   0.6

Density g/ml

Gradient column   0.9595

Infra Red   0.957, 0.958

Tensile Properties:

	In Bar Direction (6" Test Bars) (15mm) (Type I)	Perpendicular to Bar Direction (2-1/2" Test Bars) (64mm) (Type V)
Tensile Strength, PSI (MPa)		
Yield:	4743 (32.7)	4516 (31.1)
	4758 (32.8)	4526 (31.2)
Max:	4743 (32.7)	5614 (38.7)
	4758 (32.8)	5005 (34.5)
Break:	4396 (30.3)	5004 (34.5)
	3695 (25.5)	5040 (34.8)
Tensile Modulus,		
KPSI: (MPa)	611.1 (4213)	520.3 (3587)
	613.0 (4227)	513.9 (3543)
Elongation, %:		
Break	355	433
	315	400

IZOD IMPACT, ft.lb./in. of notch   (Nm/m)

	Bar Direction	Perpendicular to Bar Direction
	24.8 (1323)	26.1 (1393)
	22.0 (1174)	25.0 (1334)

EXAMPLE 10

Effect of Sequence of Heat-treatment, Cooling, Reheating to a Lower Temperature, and Pressure Recrystallization on UHMWPE.

A UHMW PE bar (3" x 15") (76 x 380mm) of the same type as in Example 1 was heated for five hours at 325°C under N$_2$, then slowly cooled to room temperature. It was reheated to 225°C, and pressure recrystallized as described in Example 9 according to the following schedule:

241° to 191°C	3000 ATM	2 hours, 15 minutes
191° to 181°C	3000 ATM	2 hours
181° to 171°C	3000 ATM	6 hours
(3000 ATM = 300 MPa)		

The resulting product was machined into test pieces and analyzed with the following results:

DSC

	Center of Bar	1 cm in from Bar Edge
m.p., °C		
1st heat	149.3	149.1
2nd heat	134.3	135.2
ΔT	15	13.9
Heat of Fusion		
1st heat	223.6 J/g	229.6 J/g
2nd heat	156.1 J/g	162.3 J/g

Infrared Crystallinity Index

In Bar Direction	0.745
Perpendicular to Bar Direction	0.759

Tensile Properties

Tensile Strength, PSI (MPa)

At Yield	4706	(32.4)	4463	(30.1)
At Break	5362	(37.0)	5326	(36.7)

```
Tensile Modulus,
    KPSI:  (MPa)    649.7  (4480)      404.2  (2787)
Elongation, %
    At Yield        4.7                    4.5
    At Break        330          ·         335
Deformation (Creep) ASTM D621 Test
    (% at 1000 psi (6.9 MPa) load)
                    0.4
                    0.3
```

Effect of Preheating by Reflux

Alternatively, the preliminary heating of Example 10 may be achieved by refluxing in vapors as described below.

A 3" x 18" (76 x 457mm) rod of UHMWLPE (American Hoechst, Hostalen GUR 415) was heated in refluxing vapors of Krytox®-143AZ (E. I. du Pont de Nemours and Company, Wilmington, Delaware) (at 333-335°C) for 2 hours, 40 minutes. Krytox®-143AZ is a perfluoroalkylpolyether that is a nonflammable, chemically inert liquid having unusually high thermal and oxidative stability. Other materials demonstrating these characteristics may also be suitable. The system was protected by a nitrogen atmosphere and was wrapped with glass insulation to facilitate slow cooling. As compared to the starting material, the resulting product has improved crystallinity (IRCI from 0.27 to 0.47), a tensile modulus (from 210 KPSI to 300 KPSI), and tensile strength at yield (from 3400 to 3850 psi (- 23.4 - 26.5 MPa). Most significantly, the product displays a large increase in elongation at break (from 315% to 893%).

When the above described material was recrystallized from 220°C under 3000 ATM, a new polyethylene resulted possessing extremely high elongation at break (667%) along with the high tensile strength at yield (4900 psi - 33.8 MPa) and the tensile modulus (574 KPSI (3958 MPa)) expected of the superior, enhanced UHMWLPE materials.

Flex Modulus, KPSI	436.4 431.2 433.80 (av)
Density	.9684
IZOD IMPACT, (ft.lb./in. of notch) (Nm/m)	17.1 (913) 15.9 (849) 16.5 (av) (881)

EXAMPLE 11

Further evidence shows that UHMWPE polymer pretreated to at least 325°C gives a superior enhanced material (SEUHMW PE).

The purpose of this Example is to show the importance of the preheat temperature.

Preheat Temperature(C°C)	225	290	310	325
Crystallinity Index	.553	.550	.605	0.76
Heat of Fusion, J/g	186	200	190	219
Tensile, Yield PSI (MPa)	4268	4277	4212	4819
Deformation (Creep)	(29.4)	(29.5)	(29.0)	(33.2)
ASTM D621 Test (% at 1000 psi (6.9 MPa) load)		0.6		0.4
IZOD ft.lb./in. of Notch (Nm/m)	20.6 (1100)	20.7 (1105)	20.6 (1100)	24 (1281)

Effect of Heating Temperature on UHMW PE

The samples were heated by placing 3/4" (19mm) cubes of UHMW polyethylene (Hoechst Hostalen GUR 415, m.w. 4-6 million, fabricated by Westlake) wrapped in Teflon® film in a large test tube protected from air with N_2. In the first experiment, a small thermocouple was inserted into the center of the cube, the purpose being to determine the time necessary for the sample to reach test temperature. A plug of glass wool was placed above the sample to control convection currents. The tube was heated with a Wood's metal bath. After the heat treatment was complete, the sample was wrapped in insulation to ensure slow cooling. At a bath temperature of 250°C, the sample required 45 minutes to reach test temperature.

Time Sample at Temperature hrs:min	Test Temperature °C	Crystallinity Index (by IR)
4:00	250	0.232
20:00	250	0.244
4:00	293	0.264
:01	293	0.230
4:00*	320-325	0.374
1:00*	334-335	0.378
1:00*	340-342	0.391

*Heated by submerging sample wrapped in Teflon® film under Woods metal as described in the following paragraph.

Effect of Time on Heating UHMW PE

Small cubes (3/4" - 19mm) of UHMW PE cut from the rod form of Hoechst Hostalen GUR 415 were wrapped in Teflon® film, tied to a glass rod, and pushed under the surface of a Wood's metal bath. In the first experiment, a small thermocouple was inserted in the cube. When plunged into a 322-329°C bath, twelve minutes were required for the sample center to reach 321°C. The time at temperature (not the time in the bath) is recorded below. The samples were removed from the bath and wrapped in glass fiber insulation to permit slow cooling which required 1.5 hours to reach 80°C. The extent of change was determined by measuring crystallinity indices.

Time Sample (at 320-325°C (hrs:min)	Crystallinity Index by (IR)
no heating	.258
0:10	.261
0:20	.294
1:00	.330
4:00	.374

Heat Treatment of UHMW PE (Large Scale)

A 3" diameter by 18" (76 x 457mm) bar of UHMW polyethylene (Hoechst Hostalen GUR 415, m.w. 4-6 million, fabrication by Westlake) was heated under nitrogen at 325°C for 4 hours (65B). The bar was cut
5 into test pieces as was a bar of the same starting polymer that had not been treated. Tests were run sequentially.

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	Untreated Polymer	Thermally Treated	% Difference
DSC		sharper (narrow curve)	
m.p.°C	139.7	137.5	
Heat of Fusion J/g	154.6	197.5	+28
Crystallinity Index (IR)	0.258	0.386	+50

Tensile Properties

Tensile Strength, psi (MPa)

Yield	3380 (23.3)	3694 (25.5)	
	3456 (23.8)	3642 (25.1)	
	3418 (23.6) (av)	3668 (25.3) (av)	+7.3
Max.	5361 (37.0)	4706 (32.4)	
	4864 (33.5)	4673 (32.2)	
	5113 (35.3) (av)	4690 (32.3) (av)	
Break	5361 (37.0)	4705 (32.4)	
	4864 (33.5)	4673 (32.2)	
	5113 (35.3) (av)	4689 (av)	

Elongation, % Break

	330	490	
	300	500	
	315 (av)	495 (av)	+57

Modulus, KPsi (MPa)	208.4 (1437)	244.6 (1687)	
	210.5 (1451)	253.7 (1749)	
	209.5 (1445) (av)	249.1 (1718) (av)	+19

Flex Modulus, KPsi (MPa)

	124.4 (858)	151.5 (1045)	
	137.1 (945)	146.8 (1012)	
	130.7 (901) (av)	149.1 (1028) (av)	+14

IZOD IMPACT, (ft.lb./in. of notch) (Nm/m)

	15.93 (850)	19.97 (1066)	
	20.81 (1111)	22.68 (1211)	
	18.37 (981) (av)	21.32 (1138) (av)	+16

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Deformation (Creep) ASTM D621 Test
(% at 1000 psi/load) *(6.9 MPa)*

1.8	1.6	-17
1.7	1.3	

Similarly, a 3" (76mm) diameter bar of different UHMW polyethylene (Himont 1900, m.w. 1,000,000) was heat pretreated in an inert atmosphere, for example, of N_2. The physical properties of the product had greatly inproved elongation and impact resistance.

	Untreated Polymer	Thermally Treated	% Difference
DSC			
Heat of Fusion J/g	166.3	190.7	+15
Crystallinity Index (IR)	.284	.379	+33
Tensile Properties			
Tensile Strength, psi (MPa)			
Yield	3544 (24.4)	3721 (25.7)	
	3703 (25.5)	3589 (24.7)	
	3622 (25.0) (av)	3655 (25.2) (av)	− 0
Max.	7387 (50.9)	6545 (45.1)	
	7190 (49.6)	5999 (41.4)	
	7289 (50.3) (av)	6272 (43.2) (av)	−14
Elongation, % Break			
	200	343	
	216	293	
	208 (av)	318 (av)	+53
% Yield	16.6	20	
	20	16.6	
Modulus, KPsi (MPa)	128.4 (885)	212.7 (1467)	
	216.2 (1491)	192.7 (1329)	
	202.7 (1398) (av)	202.7 (1398) (av)	0

IZOD IMPACT, (ft.lb./in. of notch)   (Nm/m)

```
13.05 (697)        24.26 (1295)
11.94 (637)        17.12 (914)
12.49 (656) (av)   21.09 (1126) (av)   +65
```

EXAMPLE 12

A 3" (76mm) diameter bar (rod), 18" (457mm) in length, of American Hoechst Hostalen GUR 415 ultrahigh molecular weight polyethylene, was heated in an oven and then encapsulated with low molecular weight polyethylene by rolling the hot rod onto a 1/16" (1.6mm) sheet of low molecular weight polyethylene heated to 180°C on a large hot plate. An intervening sheet of "Teflon" Polytetrofluoroethylene film was kept on the encapsulated rod to prevent sticking to the hot plate. The rod ends were similarly sealed. The "Teflon" film was kept on the encapsulated rod to prevent sticking in the reactor.

The bar was heated to 225°C under a nitrogen atmosphere and transfered to the reactor at 225°C. After sealing, the reactor pressure was taken to 3000 atmospheres which caused the temperature to reach 237°C. The reactor was permitted to cool to 180°C in 6.5 h, then maintained at this temperature for 1h. The temperature was dropped to 170°C, held at this temperature for 3h, then cooled slowly to 150°C from where it was cooled rapidly.

The rod, which remained coated, was cut and machined into two test pieces (A and B) which gave the following results:

DSC	SAMPLE	
	A	B
1st Heat:		
Melt point, °C	149.1	153.7
Heat of Fusion, J/g	219.8	209.5
2nd heat:		
Melt point, °C	135.5	136.6
Heat of fusion, J/g	141.2	144.9
Crystallinity Index (IR)	0.566	0.567
Tensile Properties:		
Tensile Strength, psi (MPa)		
At Yield	4149 (28.6)	4076 (28.1)
At Max.	7448 (51.3)	8138 (56.1)
At Break	7448 (51.3)	8138 (56.1)
Elongation, %	323	346
Modulus, Kpsi (MPa)	363.6 (2507)	358.2 (2470)
Creep Deformation, % (D621)	0.6	0.6
IZOD Impact, (ftlb/in. of notch) (Nm/m)	15.9 (849)	15.8 (843)

EXAMPLE 13

A 5.75" (146mm) segment of enhanced ultrahigh molecular weight polyethylene prepared as in Example 5, was skived to two films (A and B), of 11 mil and 5 mil thickness, respectively. The following properties were obtained (averaged from five tests per film sample):

	SAMPLE	
	A	B
Tensile Properties:		
Tensile Strength, psi (MPa)		
At Yield	3035 (20.9)	3108 (21.4)
At Max.	6554 (45.2)	4083 (28.2)
At Break	6481 (44.7)	4083 (28.2)
At 5% Elongation	2667 (18.4)	2705 (18.7)
Tensile Modulus, Kpsi (MPa)	129.7 (894)	165.6 (1142)
Elongation at Break, %	470	237.6

The skived films were hot drawn in a tenter frame at 140°C. One piece of the 5 mil film was drawn 6 fold in one direction (C). A second piece of the 5 mil film was drawn 3 fold in both directions (D):

	SAMPLE	
	C	D
Tensile Strength, psi: (MPa)		
At Yield	37,819 (261)	13,720 (95)
At Max.	42,058 (290)	19,358 (133)
At Break	46,426 (320)	18,995 (131)
Tensile Modulus, Kpsi (MPa)	93.3 (643)	94.9 (654)
Elongation at Break, %	56	132.4
Thickness, mils (μm)	2.6 (66)	1.6 (41)

CONTROL B

In this experiment, a product was prepared in the manner of Example 1 of U.S. Patent No. 3,944,536.

A sample of the ultrahigh molecular weight polyethylene used in Example 1 previously described herein, measuring 1/4" x 1/4" x 1/8" (6 x 6 x 3mm) thick was heated between a film of poly-tetrafluoroethylene on a hot plate at atmospheric pressure and at a temperature of 160°C on the upper side and 270°C on the lower side.

The molten sample was transferred quickly to a hydraulic press at room temperature where the sample was subjected to a pressure of 8 tons (about 250,000 psi or about 16,000 ATM 1600 MPa). It required 1.6 seconds to attain full pressure. The resulting polymer was tested. It displayed an infrared crystallinity index of 0.199. Its melting point was 134.5°C and, when reheated, 134.4°C.

Claims

1. An ultrahigh molecular weight linear polyethylene exhibiting a flexural modulus of 250,000-500,000 psi (1724 - 3448 MPa) a tensile stress at yield of 3500-4500 psi (24.1 - 31.0 MPa), a tensile stress at break of 4000-9000 psi (27.6 - 62.1 MPa), a tensile modulus of 300,000-700,00 psi (2069 - 4827 MPa), a notched Izod impact resistance of 12-25 ft. lb. per inch of notch (641 - 1335 Nm/m), a creep at a compression of 1000 psi (6.9 MPa) of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, a single crystalline melting point of greater than 144°C, the reduction in said melting point upon reheating being greater than 11°C and an infrared crystallinity index of at least about 0.45.

2. The composition of Claim 1 wherein the tensile modulus is 300,000-600,000 psi (2069 - 4137 MPa), the notched Izod impact resistance is 12-20 ft. lb. per inch of notch (641 - 1068 Nm/m) and the infrared crystallinity index is at least 0.5.

3. The composition of Claim 2 shaped into an article wherein its dimensions are at least one inch by at least one inch (25 x 25mm).

4. The composition of Claim 2 shaped into an article wherein its smallest dimension is at least 0.2 inch (5mm).

5. The composition of Claim 2 wherein its infrared crystallinity index is at least about 0.5.

6. An article consisting essentially of the ultrahigh molecular weight linear polyethylene of Claim 1 exhibiting a flexural modulus of 250,000-500,000 psi (1724 - 3448 MPa), a tensile stress at yield of 3500-4500 psi (24.1 - 31.0 MPa), a tensile stress at break of 4000-9000 psi (27.6 - 62.1 MPa), a tensile modulus of 300,000-700,000 psi (2069 - 4827 MPa), a notched Izod impact resistance of 12-25 ft. lb. per inch of notch (641 - 1335 Nm/m), a creep at a compression of 1000 psi (6.9 MPa) of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, a single crystalline melting point of greater than 144°C, the reduction in said melting point upon reheating being greater than 11°C and an infrared crystallinity index of at least about 0.45.

7. The shaped article of Claim 6 wherein the tensile modulus is 300,000-600,000 psi, the notched Izod impact resistance is 12-20 ft. lb. per inch of notch (641 - 1068 Nm/m) and the infrared crystallinity index is at least 0.5.

8. The shaped article of Claim 6 wherein its dimensions are at least one inch by at least one inch (25 x 25mm).

9. The shaped article of Claim 6 wherein its smallest dimension is at least 0.2 inch (5mm).

10. The shaped article of Claim 6 wherein its infrared crystallinity index is at least about 0.5.

11. A process for obtaining the ultrahigh molecular weight linear polyethylene of Claim 1 consisting essentially of the following steps:
    (a) forming said article of an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000-10,000,000;
    (b) subjecting said article to a fluid under pressure of at least 2800 ATM (280 MPa) and a temperature of 190°C-300°C;
    (c) maintaining the temperature from 190°C-300°C and the pressure of at least 2800 ATM (280 MPa) for at least 0.5 hour;
    (d) reducing the temperature to at least below 160°C-170°C while maintaining the pressure at at least 2800 ATM, the rate of reduction in temperature being such that temperature gradients in the shaped article are substantially avoided; and
    (e) cooling to a temperature of about 130°C or below and releasing the pressure to approximately 1 ATM (0.1 MPa) in a manner such that remelting of said article is prevented.

12. The process of Claim 11 wherein step (a) is performed after step (e) is performed.

13. The process of Claim 11 wherein said fluid is water.

14. The process of Claim 13 wherein said pressure in step (b) is at least 3000 ATM (300 MPa).

15. The process of Claim 13 wherein said temperature in step (b) is 200°C-230°C.

16. The process of Claim 13 wherein the temperature and pressure in step (e) is maintained for at least one hour.

17. The process of Claim 13 wherein the surface of the article is shaved after step (e).

18. The process of Claim 13 wherein the cooling rate in step (d) is no greater than 35°C per hour.

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19. The process as in Claim 13 wherein the cooling rate in step (d) is no greater than 10°C per hour.

20. An ultrahigh molecular weight linear polyethylene exhibiting a flexural modulus of 250,000-650,000 psi (1724 - 4481 MPa), a tensile stress at yield of 3500-5400 psi (24.1 - 37.2 MPa), a tensile stress at break of 4000-6000 psi (27.6 - 41.4 MPa), a tensile modulus of 300,000-700,000 psi (2069 - 4827 MPa), a notched Izod impact resistance of 12-25 ft. lb. per inch of notch (641 - 1335 Nm/m), a creep at a compression of 1000 psi (6.9 MPa) of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, a single crystalline melting point of greater than 144°C, the reduction in said melting point upon reheating being greater than 11°C and an infrared crystallinity index of at least about 0.45.

21. The composition of Claim 20 wherein the tensile modulus is 300,000-650,000 psi (2069 - 4481 MPa), the notched Izod impact resistance is 12-25 ft. lb. per inch of notch (641 - 1335 Nm/m) and the infrared crystallinity index is at least 0.5.

22. The composition of Claim 21 shaped into an article wherein its dimensions are at least one inch by at least one inch (25 x 25mm).

23. The composition of Claim 21 shaped into an article wherein its smallest dimension is at least 0.2 inch (5mm).

24. The composition of Claim 21 wherein its infrared crystallinity index is at least about 0.5.

25. An article consisting essentially of the ultrahigh molecular weight linear polyethylene of Claim 20 exhibiting a flexural modulus of 250,000-650,000 psi (1724 - 4481 MPa), a tensile stress at yield of 3500-5400 psi (24.1 - 37.2 MPa), a tensile stress at break 4000-6000 psi (27.6 - 41.4 MPa), a tensile modulus of 300,000-700,000 psi (2069 - 4827 MPa), a notched Izod impact resistance of 12-25 ft. lb. per inch of notch (641 - 1335 Nm/m), a creep at a compression of 1000 psi (6.9 MPa) of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, a single crystalline melting point of greater than 144°C, the reduction in said melting point upon reheating being greater than 11°C and an infrared crystallinity index of at least about 0.45.

26. The article of Claim 25 wherein the tensile modulus is 300,000-650,000 psi (2069 - 4481 MPa), the notched Izod impact resistance is 12-25 ft. lb. per inch of notch (641 - 1335 Nm/m) and the infrared crystallinity index is at least 0.5.

27. The article of Claim 26 wherein its dimensions are at least one inch by at least one inch (25 x 25mm).

28. The article of Claim 26 wherein its smallest dimension is at least 0.2 inch (5mm).

29. The article of Claim 25 wherein its infrared crystallinity index is at least about 0.5.

30. A process for obtaining the article of Claim 25 consisting essentially of the following steps:
  (a) forming said article of an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000-10,000,000;
  (b) subjecting said article to a preliminary heat treatment at a temperature of between 320-340°C, in an inert atmosphere for at least 0.5 hour;
  (c) subjecting said article to a fluid under pressure of at least 2800 ATM (280 MPa) and a temperature of 190°C-300°C;
  (d) maintaining the temperature from 190°C-300°C and the pressure of at least 2800 ATM (280 MPa) for at least 0.5 hour;
  (e) reducing the temperature to at least below 160°C-170°C while maintaining the pressure at at least 2800 ATM (280 MPa), the rate of reduction in temperature being such that temperature gradients in the shaped article are substantially avoided; and
  (f) cooling to a temperature of about 130°C or below and releasing the pressure to approximately 1 ATM (0.1 MPa) in a manner such that remelting of said article is prevented.

31. The process of Claim 30 wherein step (a) is performed after step (f) is performed.

32. The process of Claim 30 wherein said fluid is water.

33. The process of Claim 32 wherein said pressure in step (c) is at least 3000 ATM (300 MPa).

34. The process of Claim 32 wherein said temperature in step (c) is 200°C-230°C.

35. The process of Claim 32 wherein the temperature and pressure in step (f) is maintained for at least one hour.

36. The process of Claim 32 wherein the surface of the article is shaved after step (f).

37. The process of Claim 32 wherein the cooling rate in step (e) is no greater than 35°C per hour.

38. The process as in Claim 32 wherein the cooling rate in step (e) is no greater than 10°C per hour.

39. An improved folded chain ultrahigh molecular weight linear polyethylene exhibiting a flexural modulus of 150,000-300,000 psi (1034 - 2069 MPa), a tensile stress at yield of 3500-4000 psi (24.1 - 31.0 MPa), a tensile stress at break of 4000-6000 psi (31.0 - 41.4 MPa), a tensile modulus of 150,000-300,000 psi (1034 - 2069 MPa), a notched Izod impact resistance of 15-25 ft. lb. per inch of notch (801 - 1335 Nm/m), a creep at a compression of 1000 psi (6.9 MPa) of less than 2% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, preferably of at least 1,000,000 and an infrared crystallinity index of at least about 0.35.

40. The composition of Claim 39 wherein the elongation (% at break) is 250-900, the notched Izod impact resistance is 15-20 ft. lb. per inch of notch (801 - 1068 Nm/m).

41. The composition of Claim 39 shaped into an article wherein its dimensions are at least one inch by at least one inch (25 x 25mm).

42. The composition of Claim 39 shaped into an article wherein its smallest dimension is at least 0.2 inch (5mm).

43. An article consisting essentially of the improved folded chain ultrahigh molecular weight linear polyethylene of Claim 39 exhibiting a flexural modulus of 150,000-300,000 psi (1034 - 2069 MPa), a tensile stress at yield of 3500-4000 psi (24.1 - 31.0 MPa), a tensile stress at break of 4000-6000 psi (31.0 - 41.4 MPa), a tensile modulus of 150,000-300,000 psi (1034 - 2069 MPa), a notched Izod impact resistance of 15-25 ft. lb. per inch of notch (641 - 1335 Nm/m), a creep at a compression of 1000 psi of less than 2% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, preferably of at least 1,000,000 and an infrared crystallinity index of at least about 0.35.

44. The article of Claim 43 wherein the elongation (% at break) is 250-900, the notched Izod impact resistance is 15-20 ft. lb. per inch of notch (801 - 1068 Nm/m).

45. The article of Claim 44 wherein its dimensions are at least one inch by at least one inch (25 x 25mm).

46. The article of Claim 44 wherein its smallest dimension is at least 0.2 inch (5mm).

47. A process for obtaining the article of Claim 43 consisting essentially of the following steps:
(a) forming said article of an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000-10,000,000;
(b) subjecting said article to a temperature of 190°C-340°C for at least 0.5 hour in an inert atmosphere; and
(c) cooling the article non-precipitously to a temperature of about 130°C or below.

48. The process of Claim 47 wherein step (a) is performed after step (c) is performed.

49. The process of Claim 47 wherein said temperature in step (b) is 320°C-340°C.

50. The process of Claim 47 wherein the temperature in step (b) is maintained for at least one hour.

51. A process for producing a superior, enhanced ultrahigh molecular weight polyethylene displaying an elongation at break of at least 400% consisting essentially of the following steps:

(a) subjecting an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000 to 10,000,000 to a preliminary heat treatment of refluxing vapors at a temperature of between 320-340°C, in an inert atmosphere for at least 0.5 hour;

(b) subjecting said article to a fluid under pressure of at least 2800 ATM (280 MPa) and a temperature of 190°C-300°C;

(c) maintaining the temperature from 190°C-300°C and the pressure of at least 2800 ATM (280 MPa) for at least 0.5 hour;

(d) reducing the temperature to at least below 160°C-170°C while maintaining the pressure at at least 2800 ATM (280 MPa), the rate of reduction in temperature being such that temperature gradients in the shaped article are substantially avoided; and

(e) cooling to a temperature of about 130°C or below and releasing the pressure to approximately 1 ATM (0.1 MPa) in a manner such that remelting of said article is prevented.

52. The process of Claim 51 wherein said fluid is water.

53. The process of Claim 51 wherein said pressure in step (b) is at least 3000 ATM (300 MPa).

54. The process of Claim 51 wherein said temperature in step (b) is 200°C-230°C.

Patentansprüche

1. Lineares Polyethylen mit ultrahohem Molekulargewicht, mit einem Biegemodul von 250 000 bis 500 000 psi (1 724 bis 3 448 MPa), einer Streckspannung von 3 500 bis 4 500 psi (24,1 bis 31,0 MPa), einer Reißfestigkeit von 4 000 bis 9 000 psi (27,6 bis 62,1 MPa), einem Zugmodul von 300 000 bis 700 000 psi (2 069 bis 4 827 MPa), einer Izod-Kerbschlagzähigkeit von 12 bis 25 ft•lb/inch der Kerbe (641 bis 1 335 N•m/m), einem Kriechen bei einer Kompression von 1 000 psi (6,9 MPa) von weniger als 1 % nach 24 h bei einer Temperatur von 23 °C und einer relativen Luftfeuchtigkeit von 50 %, wobei das Polyethylen ein Molekulargewicht von 400 000 bis 10 000 000, einen einzigen Kristallschmelzpunkt von mehr als 144 °C, wobei die Erniedrigung dieses Schmelzpunkts bei erneutem Erhitzen größer als 11 °C ist, und einen Infrarot-Kristallinitäts-Index von wenigstens etwa 0,45 hat.

2. Zusammensetzung nach Anspruch 1, worin der Zugmodul 300 000 bis 600 000 psi (2 069 bis 4 137 MPa) beträgt, die Izod-Kerbschlagzähigkeit von 12 bis 20 ft•lb/inch der Kerbe (641 bis 1 068 N•m/m) beträgt und der Infrarot-Kristallinitäts-Index wenigstens 0,5 beträgt.

3. Zusammensetzung nach Anspruch 2, zu einem Gegenstand geformt, worin dessen Abmessungen wenigstens 1 inch × 1 inch (25 mm × 25 mm) betragen.

4. Zusammensetzung nach Anspruch 2, zu einem Gegenstand geformt, worin dessen kleinste Anmessung wenigstens 0,2 inch (5 mm) beträgt.

5. Zusammensetzung nach Anspruch 2, worin deren Infrarot-Kristallinitäts-Index wenigstens etwa 0,5 beträgt.

6. Gegenstand, im wesentlichen bestehend aus dem linearen Polyethylen mit ultrahohem Molekulargewicht nach Anspruch 1, mit einem Biegemodul von 250 000 bis 500 000 psi (1 724 bis 3 448 MPa), einer Streckspannung von 3 500 bis 4 500 psi (24,1 bis 31,0 MPa), einer Reißfestigkeit von 4 000 bis 9 000 psi (27,6 bis 62,1 MPa), einem Zugmodul von 300 000 bis 700 000 psi (2 069 bis 4 827 MPa), einer Izod-Kerbschlagzähigkeit von 12 bis 25 ft•lb/inch der Kerbe (641 bis 1 335 N•m/m), einem Kriechen bei einer Kompression von 1 000 psi (6,9 MPa) von weniger als 1 % nach 24 h bei einer

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Temperatur von 23 °C und einer relativen Luftfeuchtigkeit von 50 %, wobei das Polyethylen ein Molekulargewicht von 400 000 bis 10 000 000, einen einzigen Kristallschmelzpunkt von mehr als 144 °C, wobei die Erniedrigung dieses Schmelzpunkts bei erneutem Erhitzen größer als 11 °C ist, und einen Infrarot-Kristallinitäts-Index von wenigstens etwa 0,45 hat.

7. Geformter Gegenstand nach Anspruch 6, worin der Zugmodul 300 000 bis 600 000 psi (2 069 bis 4 137 MPa) beträgt, die Izod-Kerbschlagzähigkeit von 12 bis 20 ft•lb/inch der Kerbe (641 bis 1 068 N•m/m) beträgt und der Infrarot-Kristallinitäts-Index wenigstens 0,5 beträgt.

8. Geformter Gegenstand nach Anspruch 6, worin dessen Abmessungen wenigstens 1 inch x 1 inch (25 mm x 25 mm) betragen.

9. Geformter Gegenstand nach Anspruch 6, worin dessen kleinste Abmessung wenigstens 0,2 inch (5 mm) beträgt.

10. Geformter Gegenstand nach Anspruch 6, worin dessen Infrarot-Kristallinitäts-Index wenigstens etwa 0,5 beträgt.

11. Verfahren zur Herstellung des linearen Polyethylens mit ultrahohem Molekulargewicht nach Anspruch 1, im wesentlichen bestehend aus den folgenden Schritten:
    (a) Bilden des genannten Gegenstandes aus einem linearen Polyethylen mit ultrahohem Molekular-gewicht mit einem Molekulargewicht von 400 000 bis 10 000 000;
    (b) Einwirkenlassen eines fließfähigen Mediums unter einem Druck von wenigstens 2 800 ATM (280 MPa) bei einer Temperatur von 190 °C bis 300 °C auf den genannten Gegenstand;
    (c) Aufrechterhalten der Temperatur von 190 °C bis 300 °C und des Druckes von wenigstens 2 800 ATM (280 MPa) über wenigstens 0,5 h;
    (d) Erniedrigen der Temperatur auf wenigstens unterhalb von 160 °C bis 170 °C unter Aufrechter-halten des Druckes von wenigstens 2 800 ATM (280 MPa), wobei die Geschwindigkeit der Temperaturerniedrigung so ist, daß Temperaturgradienten in dem geformten Gegenstand im wesent-lichen vermieden werden; und
    (e) Abkühlen auf eine Temperatur von etwa 130 °C oder darunter und Druckablassen auf etwa 1 ATM (0,1 MPa) in solcher Weise, daß ein erneutes Schmelzen des Gegenstandes verhindert wird.

12. Verfahren nach Anspruch 11, worin der Schritt (a) durchgeführt wird, nachdem der Schritt (e) durchgeführt worden ist.

13. Verfahren nach Anspruch 11, worin das fließfähige Medium Wasser ist.

14. Verfahren nach Anspruch 13, worin der Druck in Schritt (b) wenigstens 3 000 ATM (300 MPa) beträgt.

15. Verfahren nach Anspruch 13, worin die Temperatur in Schritt (b) 200 °C bis 230 °C beträgt.

16. Verfahren nach Anspruch 13, worin die Temperatur und der Druck in Schritt (e) wenigstens 1 h aufrechterhalten werden.

17. Verfahren nach Anspruch 13, worin die Oberfläche des Gegenstandes nach dem Schritt (e) abgeschabt wird.

18. Verfahren nach Anspruch 13, worin die Geschwindigkeit der Abkühlung in Schritt (d) nicht größer als 35 °C/h ist.

19. Verfahren nach Anspruch 13, worin die Geschwindigkeit der Abkühlung in Schritt (d) nicht größer als 10 °C/h ist.

20. Lineares Polyethylen mit ultrahohem Molekulargewicht, mit einem Biegemodul von 250 000 bis 650 000 psi (1 724 bis 4 481 MPa), einer Streckspannung von 3 500 bis 5 400 psi (24,1 bis 37,2 MPa), einer Reißfestigkeit von 4 000 bis 6 000 psi (27,6 bis 41,4 MPa), einem Zugmodul von 300 000 bis 700 000 psi (2 069 bis 4 827 MPa), einer Izod-Kerbschlagzähigkeit von 12 bis 25 ft•lb/inch der Kerbe (641 bis 1

335 N•m/m), einem Kriechen bei einer Kompression von 1 000 psi (6,9 MPa) von weniger als 1 % nach 24 h bei einer Temperatur von 23 °C und einer relativen Luftfeuchtigkeit von 50 %, wobei das Polyethylen ein Molekulargewicht von 400 000 bis 10 000 000, einen einzigen Kristallschmelzpunkt von mehr als 144 °C, wobei die Erniedrigung dieses Schmelzpunkts bei erneutem Erhitzen größer als 11 °C ist, und einen Infrarot-Kristallinitäts-Index von wenigstens etwa 0,45 hat.

21. Zusammensetzung nach Anspruch 20, worin der Zugmodul 300 000 bis 650 000 psi (2 069 bis 4 481 MPa) beträgt, die Izod-Kerbschlagzähigkeit von 12 bis 25 ft•lb/inch der Kerbe (641 bis 1 335 N•m/m) beträgt und der Infrarot-Kristallinitäts-Index wenigstens 0,5 beträgt.

22. Zusammensetzung nach Anspruch 21, zu einem Gegenstand geformt, worin dessen Abmessungen wenigstens 1 inch x 1 inch (25 mm x 25 mm) betragen.

23. Zusammensetzung nach Anspruch 21, zu einem Gegenstand geformt, worin dessen kleinste Abmessung wenigstens 0,2 inch (5 mm) beträgt.

24. Zusammensetzung nach Anspruch 21, worin deren Infrarot-Kristallinitäts-Index wenigstens etwa 0,5 beträgt.

25. Gegenstand, im wesentlichen bestehend aus dem linearen Polyethylen mit ultrahohem Molekulargewicht nach Anspruch 20, mit einem Biegemodul von 250 000 bis 650 000 psi (1 724 bis 4 481 MPa), einer Streckspannung von 3 500 bis 5 400 psi (24,1 bis 41,4 MPa), einer Reißfestigkeit von 4 000 bis 6 000 psi (27,6 bis 41,4 MPa), einem Zugmodul von 300 000 bis 700 000 psi (2 069 bis 4 827 MPa), einer Izod-Kerbschlagzähigkeit von 12 bis 25 ft•lb/inch der Kerbe (641 bis 1 335 N•m/m), einem Kriechen bei einer Kompression von 1 000 psi (6,9 MPa) von weniger als 1 % nach 24 h bei einer Temperatur von 23 °C und einer relativen Luftfeuchtigkeit von 50 %, wobei das Polyethylen ein Molekulargewicht von 400 000 bis 10 000 000, einen einzigen Kristallschmelzpunkt von mehr als 144 °C, wobei die Erniedrigung dieses Schmelzpunkts bei erneutem Erhitzen größer als 11 °C ist, und einen Infrarot-Kristallinitäts-Index von wenigstens etwa 0,45 hat.

26. Geformter Gegenstand nach Anspruch 25, worin der Zugmodul 300 000 bis 650 000 psi (2 069 bis 4 481 MPa) beträgt, die Izod-Kerbschlagzähigkeit von 12 bis 25 ft•lb/inch der Kerbe (641 bis 1 335 N•m/m) beträgt und der Infrarot-Kristallinitäts-Index wenigstens 0,5 beträgt.

27. Geformter Gegenstand nach Anspruch 26, worin dessen Abmessungen wenigstens 1 inch x 1 inch (25 mm x 25 mm) betragen.

28. Geformter Gegenstand nach Anspruch 26, worin dessen kleinste Abmessung wenigstens 0,2 inch (5 mm) beträgt.

29. Geformter Gegenstand nach Anspruch 25, worin dessen Infrarot-Kristallinitäts-Index wenigstens etwa 0,5 beträgt.

30. Verfahren zur Herstellung des linearen Polyethylens mit ultrahohem Molekulargewicht nach Anspruch 25, im wesentlichen bestehend aus den folgenden Schritten:
    (a) Bilden des genannten Gegenstandes aus einem linearen Polyethylen mit ultrahohem Molekulargewicht mit einem Molekulargewicht von 400 000 bis 10 000 000;
    (b) Einwirkenlassen einer vorherigen Wärmebehandlung von wenigstens etwa 0,5 h bei einer Temperatur zwischen 320 °C und 340 °C in einer inerten Atmosphäre auf den genannten Gegenstand;
    (c) Einwirkenlassen eines fließfähigen Mediums unter einem Druck von wenigstens 2 800 ATM (280 MPa) bei einer Temperatur von 190 °C bis 300 °C auf den genannten Gegenstand;
    (d) Aufrechterhalten der Temperatur von 190 °C bis 300 °C und des Druckes von wenigstens 2 800 ATM (280 MPa) über wenigstens 0,5 h;
    (e) Erniedrigen der Temperatur auf wenigstens unterhalb von 160 °C bis 170 °C unter Aufrechterhalten des Druckes von wenigstens 2 800 ATM (280 MPa), wobei die Geschwindigkeit der Temperaturerniedrigung so ist, daß Temperaturgradienten in dem geformten Gegenstand im wesentlichen vermieden werden; und

(f) Abkühlen auf eine Temperatur von etwa 130 °C oder darunter und Druckablassen auf etwa 1 ATM (0,1 MPa) in solcher Weise, daß ein erneutes Schmelzen des Gegenstandes verhindert wird.

31. Verfahren nach Anspruch 30, worin der Schritt (a) durchgeführt wird, nachdem der Schritt (f) durchgeführt worden ist.

32. Verfahren nach Anspruch 30, worin das fließfähige Medium Wasser ist.

33. Verfahren nach Anspruch 32, worin der Druck in Schritt (c) wenigstens 3 000 ATM (300 MPa) beträgt.

34. Verfahren nach Anspruch 32, worin die Temperatur in Schritt (c) 200 °C bis 230 °C beträgt.

35. Verfahren nach Anspruch 32, worin die Temperatur und der Druck in Schritt (f) wenigstens 1 h aufrechterhalten werden.

36. Verfahren nach Anspruch 32, worin die Oberfläche des Gegenstandes nach dem Schritt (f) abgeschabt wird.

37. Verfahren nach Anspruch 32, worin die Geschwindigkeit der Abkühlung in Schritt (e) nicht größer als 35 °C/h ist.

38. Verfahren nach Anspruch 32, worin die Geschwindigkeit der Abkühlung in Schritt (e) nicht größer als 10 °C/h ist.

39. Verbessertes lineares Polyethylen mit gefalteter Kette und mit ultrahohem Molekulargewicht, mit einem Biegemodul von 150 000 bis 300 000 psi (1 034 bis 2 069 MPa) , einer Streckspannung von 3 500 bis 4 000 psi (24,1 bis 27,6 MPa), einer Reißfestigkeit von 4 000 bis 6 000 psi (27,6 bis 41,4 MPa), einem Zugmodul von 150 000 bis 300 000 psi (1 034 bis 2 069 MPa), einer Izod-Kerbschlagzähigkeit von 15 bis 25 ft•lb/inch der Kerbe (801 bis 1 335 N•m/m), einem Kriechen bei einer Kompression von 1 000 psi (6,9 MPa) von weniger als 2 % nach 24 h bei einer Temperatur von 23 °C und einer relativen Luftfeuchtigkeit von 50 %, wobei das Polyethylen ein Molekulargewicht von 400 000 bis 10 000 000, vorzugsweise von wenigstens 1 000 000, und einen Infrarot-Kristallinitäts-Index von wenigstens etwa 0,35 hat.

40. Zusammensetzung nach Anspruch 39, worin die prozentuale Reißdehnung 250 bis 900 beträgt, die Izod-Kerbschlagzähigkeit von 15 bis 20 ft•lb/inch der Kerbe (801 bis 1 068 N•m/m) beträgt.

41. Zusammensetzung nach Anspruch 39, zu einem Gegenstand geformt, worin dessen Abmessungen wenigstens 1 inch x 1 inch (25 mm x 25 mm) betragen.

42. Zusammensetzung nach Anspruch 39, zu einem Gegenstand geformt, worin dessen kleinste Abmessung wenigstens 0,2 inch (5 mm) beträgt.

43. Gegenstand, im wesentlichen bestehend aus dem verbesserten linearen Polyethylen mit gefalteter Kette und mit ultrahohem Molekulargewicht nach Anspruch 39, mit einem Biegemodul von 150 000 bis 300 000 psi (1 034 bis 2 069 MPa), einer Streckspannung von 3 500 bis 4 000 psi (24,1 bis 27,6 MPa), einer Reißfestigkeit von 4 000 bis 6 000 psi (27,6 bis 41,4 MPa), einem Zugmodul von 150 000 bis 300 000 psi (1 034 bis 2 069 MPa), einer Izod-Kerbschlagzähigkeit von 15 bis 25 ft•lb/inch der Kerbe (801 bis 1 335 N•m/m), einem Kriechen bei einer Kompression von 1 000 psi (6,9 MPa) von weniger als 1 % nach 24 h bei einer Temperatur von 23 °C und einer relativen Luftfeuchtigkeit von 50 %, wobei das Polyethylen ein Molekulargewicht von 400 000 bis 10 000 000, vorzugsweise von wenigstens 1 000 000, und einen Infrarot-Kristallinitäts-Index von wenigstens etwa 0,35 hat.

44. Geformter Gegenstand nach Anspruch 43, worin die prozentuale Reißdehnung 250 bis 900 beträgt, die Izod-Kerbschlagzähigkeit von 15 bis 20 ft•lb/inch der Kerbe (801 bis 1 068 N•m/m) beträgt.

45. Geformter Gegenstand nach Anspruch 44, worin dessen Abmessungen wenigstens 1 inch x 1 inch (25 mm x 25 mm) betragen.

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46. Geformter Gegenstand nach Anspruch 44, worin dessen kleinste Abmessung wenigstens 0,2 inch (5 mm) beträgt.

47. Verfahren zur Herstellung des Gegenstandes nach Anspruch 43, im wesentlichen bestehend aus den folgenden Schritten:

(a) Bilden des genannten Gegenstandes aus einem linearen Polyethylen mit ultrahohem Molekulargewicht mit einem Molekulargewicht von 400 000 bis 10 000 000;

(b) Einwirkenlassen einer Temperatur von 190 °C bis 340 °C in einer inerten Atmosphäre auf den Gegenstand über wenigstens 0,5 h;

(c) nicht-überstürztes Abkühlenlassen des Gegenstandes auf eine Temperatur von etwa 130 °C oder darunter.

48. Verfahren nach Anspruch 47, worin der Schritt (a) durchgeführt wird, nachdem der Schritt (c) durchgeführt worden ist.

49. Verfahren nach Anspruch 47, worin die Temperatur in Schritt (b) 320 °C bis 340 °C beträgt.

50. Verfahren nach Anspruch 47, worin die Temperatur in Schritt (b) wenigstens 1 h aufrechterhalten wird.

51. Verfahren zur Herstellung eines überlegenen, verstärkten Polyethylens mit ultrahohem Molekulargewicht und mit einer Reißdehnung von wenigstens 400 %, im wesentlichen bestehend aus den folgenden Schritten:

(a) Einwirkenlassen einer vorherigen Wärmebehandlung von wenigstens etwa 0,5 h durch zurückfließende Dämpfe bei einer Temperatur zwischen 320 °C und 340 °C in einer inerten Atmosphäre auf das lineare Polyethylen mit ultrahohem Molekulargewicht mit einem Molekulargewicht von 400 000 bis 10 000 000;

(b) Einwirkenlassen eines fließfähigen Mediums unter einem Druck von wenigstens 2 800 ATM (280 MPa) bei einer Temperatur von 190 °C bis 300 °C auf den genannten Gegenstand;

(c) Aufrechterhalten der Temperatur von 190 °C bis 300 °C und des Druckes von wenigstens 2 800 ATM (280 MPa) über wenigstens 0,5 h;

(d) Erniedrigen der Temperatur auf wenigstens unterhalb von 160 °C bis 170 °C unter Aufrechterhalten des Druckes von wenigstens 2 800 ATM (280 MPa), wobei die Geschwindigkeit der Temperaturerniedrigung so ist, daß Temperaturgradienten in dem geformten Gegenstand im wesentlichen vermieden werden; und

(e) Abkühlen auf eine Temperatur von etwa 130 °C oder darunter und Druckablassen auf etwa 1 ATM (0,1 MPa) in solcher Weise, daß ein erneutes Schmelzen des Gegenstandes verhindert wird.

52. Verfahren nach Anspruch 51, worin das fließfähige Medium Wasser ist.

53. Verfahren nach Anspruch 51, worin der Druck in Schritt (c) wenigstens 3 000 ATM (300 MPa) beträgt.

54. Verfahren nach Anspruch 51, worin die Temperatur in Schritt (b) 200 °C bis 230 °C beträgt.

Revendications

1. Un polyéthylène linéaire à poids moléculaire ultra-élevé présentant un module en flexion de 1724 à 3448 MPa, une limite d'élasticité à la traction de 24,1 à 31,0 MPa, une limite de rupture à la traction de 27,6 à 62,1 MPa, un module en traction de 2069 à 4827 MPa, une résistance au choc Izod avec entaille de 641 à 1335 nm/m d'entaille, un fluage sous une compression de 6,9 MPa inférieur à 1 % après 24 heures à une température de 23 °C et une humidité relative de 50 %, le polyéthylène ayant un poids moléculaire de 400 000 à 10 000 000, un seul point de fusion cristalline supérieur à 144 °C, l'abaissement dudit point de fusion par réchauffage étant supérieur à 11 °C, et un indice de cristallinité par analyse aux infrarouges d'au moins environ 0,45.

2. La composition de la revendication 1, dans laquelle le module en traction est de 2069 à 4137 MPa, la résistance au choc Izod avec entaille est de 641 à 1068 nm/m d'entaille et l'indice de cristallinité par analyse aux infrarouges est d'au moins 0,5.

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3. La composition de la revendication 2, façonnée en un article dont les dimensions sont d'au moins 25 mm sur au moins 25 mm.

4. La composition de la revendication 2, façonnée en un article dont la plus petite dimension est d'au moins 5 mm.

5. La composition de la revendication 2, dont l'indice de cristallinité par analyse aux infrarouges est d'au moins environ 0,5.

6. Un article constitué essentiellement du polyéthylène linéaire à poids moléculaire ultra-élevé de la revendication 1, présentant un module en flexion de 1724 à 3448 MPa, une limite d'élasticité à la traction de 24,1 à 31,0 MPa, une limite de rupture à la traction de 27,6 à 62,1 MPa, un module en traction de 2069 à 4827 MPa, une résistance au choc Izod avec entaille de 641 à 1335 nm/m d'entaille, un fluage sous une compression de 6,9 MPa inférieur à 1 % après 24 heures à une température de 23°C et une humidité relative de 50 %, le polyéthylène ayant un poids moléculaire de 400 000 à 10 000 000, un seul point de fusion cristalline supérieur à 144°C, l'abaissement dudit point de fusion par réchauffage étant supérieur à 11°C, et un indice de cristallinité par analyse aux infrarouges d'au moins environ 0,45.

7. L'article façonné de la revendication 6, dans lequel le module en traction est de 2069 à 4137 MPa, la résistance au choc Izod avec entaille est de 641 à 1068 nm/m d'entaille et l'indice de cristallinité par analyse aux infrarouges est d'au moins 0,5.

8. L'article façonné de la revendication 6, dont les dimensions sont d'au moins 25 mm sur au moins 25 mm.

9. L'article façonné de la revendication 6, dont la plus petite dimension est d'au moins 5 mm.

10. L'article façonné de la revendication 6, dont l'indice de cristallinité par analyse aux infrarouges est d'au moins environ 0,5.

11. Un procédé pour obtenir le polyéthylène linéaire à poids moléculaire ultra-élevé de la revendication 1, qui se compose essentiellement des étapes suivantes :
    (a) former ledit article constitué d'un polyéthylène linéaire à poids moléculaire ultra-élevé ayant un poids moléculaire de 400 000 à 10 000 000 ;
    (b) soumettre ledit article à un fluide sous une pression d'au moins 280 MPa et à une température de 190°C à 300°C ;
    (c) maintenir la température de 190°C à 300°C et la pression d'au moins 280 MPa pendant au moins 0,5 heure ;
    (d) abaisser la température au moins jusqu'au-dessous de 160°C à 170°C tout en maintenant la pression à au moins 280 MPa, la vitesse d'abaissement de la température étant telle que des gradients de température dans l'article façonné soient sensiblement évités ; et
    (e) refroidir jusqu'à une température d'environ 130°C ou moins et relâcher la pression jusqu'à environ 0,1 MPa de telle manière que soit empêchée une refonte dudit article.

12. Le procédé de la revendication 11, dans lequel l'étape (a) est exécutée après l'exécution de l'étape (e).

13. Le procédé de la revendication 11, dans lequel ledit fluide est l'eau.

14. Le procédé de la revendication 13, dans lequel ladite pression dans l'étape (b) est d'au moins 300 MPa.

15. Le procédé de la revendication 13, dans lequel ladite température dans l'étape (b) est de 200°C à 230°C.

16. Le procédé de la revendication 13, dans lequel la température et la pression dans l'étape (e) sont maintenues pendant au moins une heure.

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17. Le procédé de la revendication 13, dans lequel la surface de l'article est pelée après l'étape (e).

18. Le procédé de la revendication 13, dans lequel la vitesse de refroidissement dans l'étape (d) n'est pas supérieure à 35°C par heure.

19. Le procédé de la revendication 13, dans lequel la vitesse de refroidissement dans l'étape (d) n'est pas supérieure à 10°C par heure.

20. Un polyéthylène linéaire à poids moléculaire ultra-élevé présentant un module en flexion de 1724 à 4481 MPa, une limite d'élasticité à la traction de 24,1 à 37,2 MPa, une limite de rupture à la traction de 27,6 à 41,4 MPa, un module en traction de 2069 à 4827 MPa, une résistance au choc Izod avec entaille de 641 à 1335 nm/m d'entaille, un fluage sous une compression de 6,9 MPa inférieur à 1 % après 24 heures à une température de 23°C et une humidité relative de 50 %, le polyéthylène ayant un poids moléculaire de 400 000 à 10 000 000, un seul point de fusion cristalline supérieur à 144°C, l'abaissement dudit point de fusion par réchauffage étant supérieur à 11°C, et un indice de cristallinité par analyse aux infrarouges d'au moins environ 0,45.

21. La composition de la revendication 20, dans laquelle le module en traction est de 2069 à 4481 MPa, la résistance au choc Izod avec entaille est de 641 à 1335 nm/m d'entaille et l'indice de cristallinité par analyse aux infrarouges est d'au moins 0,5.

22. La composition de la revendication 21, façonnée en un article dont les dimensions sont d'au moins 25 mm sur au moins 25 mm.

23. La composition de la revendication 21, façonnée en un article dont la plus petite dimension est d'au moins 5 mm.

24. La composition de la revendication 21, dont l'indice de cristallinité par analyse aux infrarouges est d'au moins environ 0,5.

25. Un article constitué essentiellement du polyéthylène linéaire à poids moléculaire ultra-élevé de la revendication 20, présentant un module en flexion de 1724 à 4481 MPa, une limite d'élasticité à la traction de 24,1 à 37,2 MPa, une limite de rupture à la traction de 27,6 à 41,4 MPa, un module en traction de 2069 à 4827 MPa, une résistance au choc Izod avec entaille de 641 à 1335 nm/m d'entaille, un fluage sous une compression de 6,9 MPa inférieur à 1 % après 24 heures à une température de 23°C et une humidité relative de 50 %, le polyéthylène ayant un poids moléculaire de 400 000 à 10 000 000, un seul point de fusion cristalline supérieur à 144°C, l'abaissement dudit point de fusion par réchauffage étant supérieur à 11°C, et un indice de cristallinité par analyse aux infrarouges d'au moins environ 0,45.

26. L'article de la revendication 25, dans lequel le module en traction est de 2069 à 4481 MPa, la résistance au choc Izod avec entaille est de 641 à 1335 nm/m d'entaille et l'indice de cristallinité par analyse aux infrarouges est d'au moins 0,5.

27. L'article de la revendication 26, dont les dimensions sont d'au moins 25 mm sur au moins 25 mm.

28. L'article de la revendication 26, dont la plus petite dimension est d'au moins 5 mm.

29. L'article de la revendication 25, dont l'indice de cristallinité par analyse aux infrarouges est d'au moins environ 0,5.

30. Un procédé pour obtenir l'article de la revendication 25, qui se compose essentiellement des étapes suivantes :
(a) former ledit article constitué d'un polyéthylène linéaire à poids moléculaire ultra-élevé ayant un poids moléculaire de 400 000 à 10 000 000 ;
(b) soumettre ledit article à un traitement thermique préliminaire à une température comprise entre 320 et 340°C dans une atmosphère inerte pendant au moins 0,5 heure ;

(c) soumettre ledit article à un fluide sous une pression d'au moins 280 MPa et à une température de 190°C à 300°C ;

(d) maintenir la température de 190°C à 300°C et la pression d'au moins 280 MPa pendant au moins 0,5 heure ;

5   (e) abaisser la température au moins jusqu'au-dessous de 160°C à 170°C tout en maintenant la pression à au moins 280 MPa, la vitesse d'abaissement de la température étant telle que des gradients de température dans l'article façonné soient sensiblement évités ; et

(f) refroidir jusqu'à une température d'environ 130°C ou moins et relâcher la pression jusqu'à environ 0,1 MPa de telle manière que soit empêchée une refonte dudit article.

10

31. Le procédé de la revendication 30, dans lequel l'étape (a) est exécutée après l'exécution de l'étape (f).

32. Le procédé de la revendication 30, dans lequel ledit fluide est l'eau.

15   33. Le procédé de la revendication 32, dans lequel ladite pression dans l'étape (c) est d'au moins 300 MPa.

34. Le procédé de la revendication 32, dans lequel ladite température dans l'étape (c) est de 200°C à 230°C.

20

35. Le procédé de la revendication 32, dans lequel la température et la pression dans l'étape (f) sont maintenues pendant au moins une heure.

36. Le procédé de la revendication 32, dans lequel la surface de l'article est pelée après l'étape (f).

25

37. Le procédé de la revendication 32, dans lequel la vitesse de refroidissement dans l'étape (e) n'est pas supérieure à 35°C par heure.

38. Le procédé de la revendication 32, dans lequel la vitesse de refroidissement dans l'étape (e) n'est pas
30   supérieure à 10°C par heure.

39. Un polyéthylène linéaire à poids moléculaire ultra-élevé à chaîne repliée amélioré présentant un module en flexion de 1034 à 2069 MPa, une limite d'élasticité à la traction de 24,1 à 31,0 MPa, une limite de rupture à la traction de 31,0 à 41,4 MPa, un module en traction de 1034 à 2069 MPa, une
35   résistance au choc Izod avec entaille de 801 à 1335 nm/m d'entaille, un fluage sous une compression de 6,9 MPa inférieur à 2 % après 24 heures à une température de 23°C et une humidité relative de 50 %, le polyéthylène ayant un poids moléculaire de 400 000 à 10 000 000, de préférence d'au moins 1 000 000, et un indice de cristallinité par analyse aux infrarouges d'au moins environ 0,35.

40   40. La composition de la revendication 39, dans laquelle l'allongement (% à la rupture) est de 250 à 900, la résistance au choc Izod avec entaille est de 801 à 1068 nm/m d'entaille.

41. La composition de la revendication 39, façonnée en un article dont les dimensions sont d'au moins 25 mm sur au moins 25 mm.

45

42. La composition de la revendication 39, façonnée en un article dont la plus petite dimension est d'au moins 5 mm.

43. Un article constitué essentiellement du polyéthylène linéaire à poids moléculaire ultra-élevé à chaîne
50   repliée amélioré de la revendication 39, présentant un module en flexion de 1034 à 2069 MPa, une limite d'élasticité à la traction de 24,1 à 31,0 MPa, une limite de rupture à la traction de 31,0 à 41,4 MPa, un module en traction de 1034 à 2069 MPa, une résistance au choc Izod avec entaille de 801 à 1335 nm/m d'entaille, un fluage sous une compression de 6,9 MPa inférieur à 2 % après 24 heures à une température de 23°C et une humidité relative de 50 %, le polyéthylène ayant un poids moléculaire
55   de 400 000 à 10 000 000, de préférence d'au moins 1 000 000, et un indice de cristallinité par analyse aux infrarouges d'au moins environ 0,35.

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44. L'article de la revendication 43, dans lequel l'allongement (% à la rupture) est de 250 à 900, la résistance au choc Izod avec entaille est de 801 à 1068 nm/m d'entaille.

45. L'article de la revendication 44, dont les dimensions sont d'au moins 25 mm sur au moins 25 mm.

46. L'article de la revendication 44, dont la plus petite dimension est d'au moins 5 mm.

47. Un procédé pour obtenir l'article de la revendication 43, qui se compose essentiellement des étapes suivantes :

(a) former ledit article constitué d'un polyéthylène linéaire à poids moléculaire ultra-élevé ayant un poids moléculaire de 400 000-10 000 000 ;

(b) soumettre ledit article à une température de 190°C à 340°C pendant au moins 0,5 heure dans une atmosphère inerte ; et

(c) refroidir l'article sans hâte jusqu'à une température d'environ 130°C ou moins.

48. Le procédé de la revendication 47, dans lequel l'étape (a) est exécutée après l'exécution de l'étape (c).

49. Le procédé de la revendication 47, dans lequel ladite température dans l'étape (b) est de 320°C à 340°C.

50. Le procédé de la revendication 47, dans lequel la température dans l'étape (b) est maintenue pendant au moins une heure.

51. Un procédé pour produire un polyéthylène à poids moléculaire ultra-élevé amélioré, supérieur, présentant un allongement à la rupture d'au moins 400 %, qui se compose essentiellement des étapes suivantes :

(a) soumettre un polyéthylène linéaire à poids moléculaire ultra-élevé ayant un poids moléculaire de 400 000 à 10 000 000 à un traitement thermique préliminaire par des vapeurs au reflux à une température comprise entre 320 et 340°C dans une atmosphère inerte pendant au moins 0,5 heure ;

(b) soumettre ledit article à un fluide sous une pression d'au moins 280 MPa et à une température de 190°C à 300°C ;

(c) maintenir la température de 190°C à 300°C et la pression d'au moins 280 MPa pendant au moins 0,5 heure ;

(d) abaisser la température au moins jusqu'au-dessous de 160°C à 170°C tout en maintenant la pression à au moins 280 MPa, la vitesse d'abaissement de la température étant telle que des gradients de température dans l'article façonné soient sensiblement évités ; et

(e) refroidir jusqu'à une température d'environ 130°C ou moins et relâcher la pression jusqu'à environ 0,1 MPa de telle manière que soit empêchée une refonte dudit article.

52. Le procédé de la revendication 51, dans lequel ledit fluide est l'eau.

53. Le procédé de la revendication 51, dans lequel ladite pression dans l'étape (b) est d'au moins 300 MPa.

54. Le procédé de la revendication 51, dans lequel ladite température dans l'étape (b) est de 200°C à 230°C.
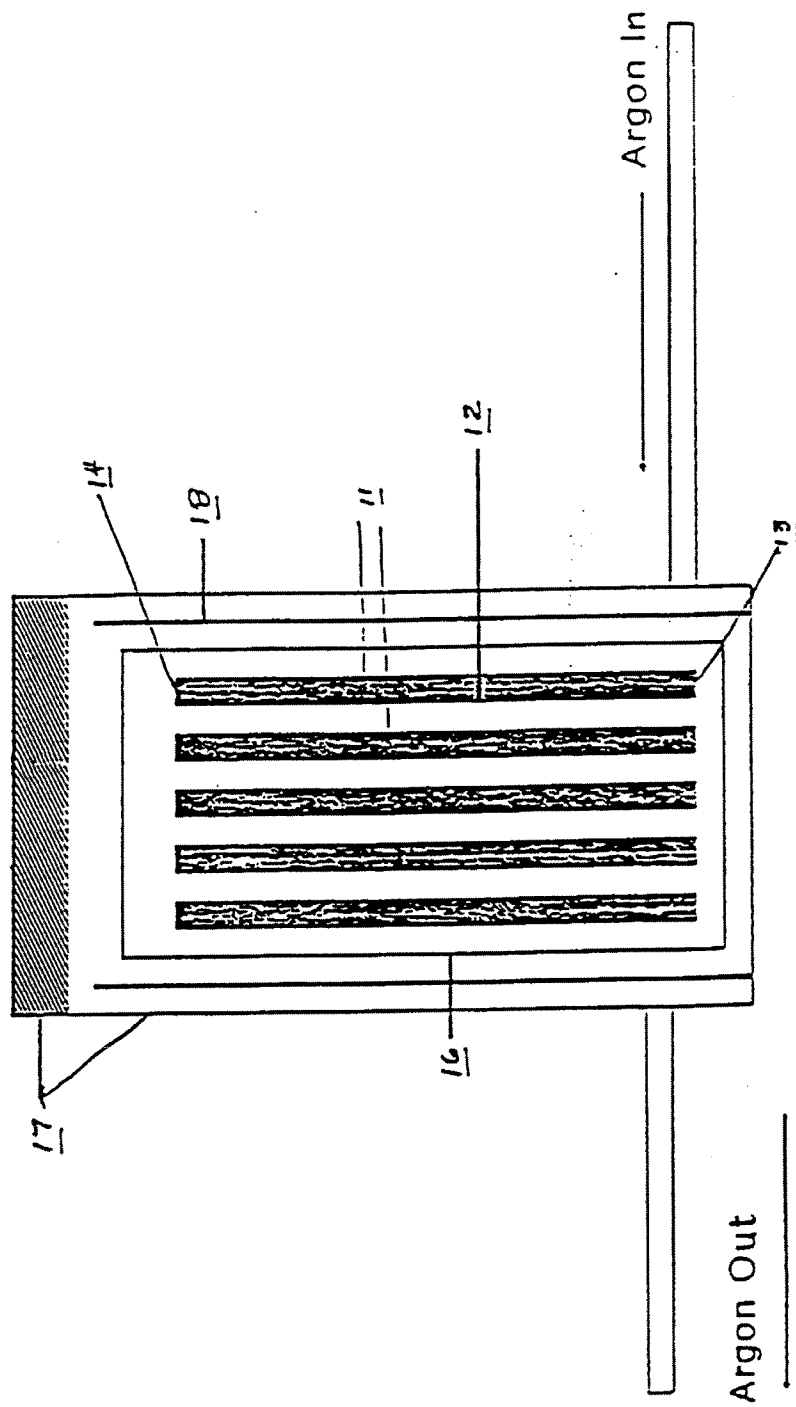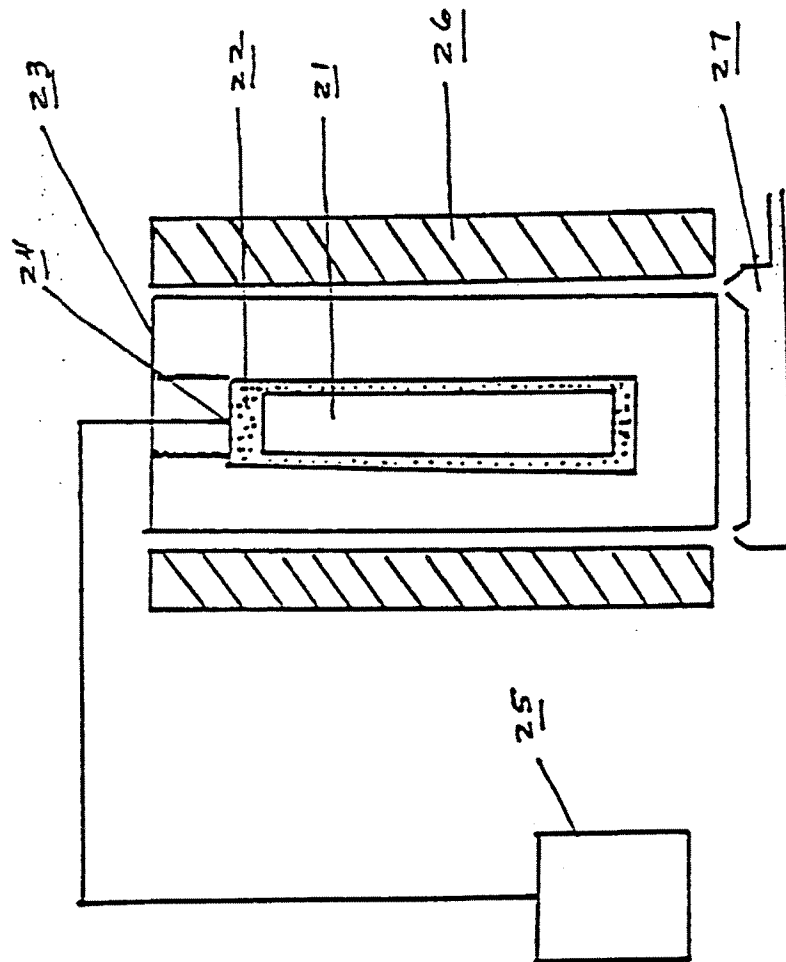
32

FIGURE 1

Argon In

Argon Out

FIGURE 2

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(54) Process of manufacturing ultrahigh molecular weight linear polyethylene shaped articles.

(57) A novel process for preparing an ultrahigh molecular weight linear polyethylene (UHMWLPE) in the form of a shaped article exhibiting a unique combination of properties is disclosed.

FIGURE 1
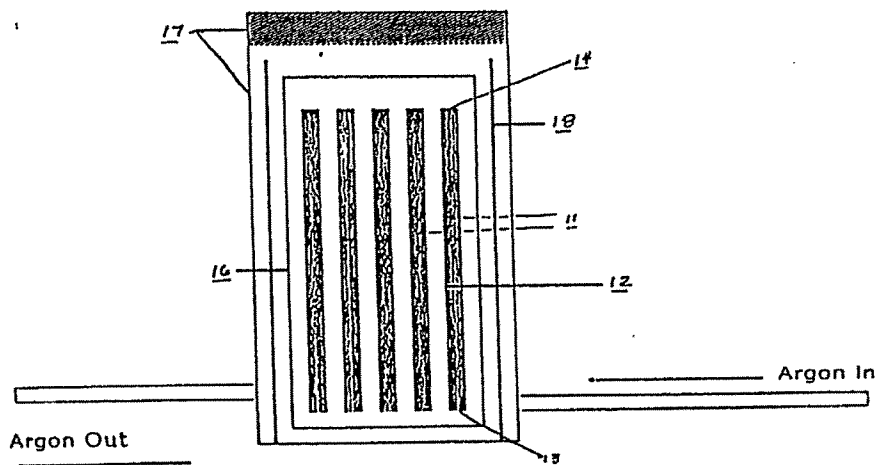
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PROCESS OF MANUFACTURING ULTRAHIGH MOLECULAR WEIGHT LINEAR POLYETHYLENE SHAPED ARTICLES

CROSS-REFERENCE TO RELATED APPLICATION

5   This application is a continuation-in-part of my co-pending application U.S. Serial No. 07/426,918 filed October 24, 1989 which in turn is a continuation-in-part of U.S. Serial No. 07/288,576 filed December 22, 1988, which in turn is a continuation-in-part of my co-pending application U.S. Serial No. 07/278,912 filed December 2, 1988.

10   ## BACKGROUND OF THE INVENTION

1. Field of the Invention

15   This invention relates to a novel process for making ultrahigh molecular weight linear polyethylene (UHMWLPE). This novel UHMWLPE, in the form of a shaped article, exhibits a unique combination of properties making the material useful as a bearing surface, in general, but particularly useful as a prosthetic hip joint cup and as other prosthetic shapes for replacement of other joints of the human body. This article
20   is the subject of copending U.S. patent application (DE-0284C) filed to E. G. Howard on November   , 1989 which is a continuation-in-part of U.S. Serial No. 07/426,916 filed on October 24, 1989 which is a continuation-in-part of co-pending U.S. Serial No. 07/288,577 filed December 22, 1988, which in turn is a continuation-in-part of co-pending U.S. Serial No. 07/278,913, filed December 2, 1988.

25   2. Description of the Prior Art

In U.S. Patent No. 3,944,536 (March 1976), Lupton et al describe UHMWPE in the form of a fabricated article exhibiting an elastic modulus of 340,000 to 500,000 psi, a tensile impact strength of 140 to 600 ft
30   lb/in², a density of 0.95 to 0.98 g/cc at 25° C, a crystalline melting point of 142 to 148° C (as measured by differential thermal analysis) and a unique crystalline form characterized by the absence of fold spacings of 50-2000 Angstrom units (Å) and the presence of crystal spacings of about 10,000 Å. The critical feature of the process of producing this UHMWPE is disclosed to involve inducing crystallization of the molten polymer above 150° C by rapidly increasing the applied pressure from an initial level of 1 to 1000
35   atmospheres to a second level of 2000 to 7000 atmospheres and then cooling rapidly while maintaining a pressure sufficient to maintain the polyethylene in the solid phase until the temperature is below the crystalline melting point of the polyethylene at atmospheric pressure.

In Kunstuffe German Plastics 77 (1987) pp. 617-622, in an article entitled "Ultrahigh Molecular Polyethylene for Replacement Joints", Eyrer et al. point out that the service life of joint replacements made
40   of UHMWPE is limited. Analysis of the damage to over 250 explanted hip cups and tibial plateaus revealed a changed property profile which they explained by post-crystallization resulting from oxidative chain decomposition. They suggested optimizing the processing of polyethylene under higher pressure and higher temperature to increase the degree of crystallinity. The Eyrer et al. product displays a creep of above 5% at a compression of 1000 psi (6.9 M/mm²) for 24 hours at 37° C.

45   One of the most remarkable advances in the medical field in recent years is the development of prosthetic joints, particularly the load bearing hip. The crippled and sometimes bed ridden elderly can walk again. The key to this development is UHMWPE because, not only does it have the necessary impact strength, but it initiates no adverse blood reactions. But at present, these prosthetic joints are limited to the older, less active segment of the population because the polymer tends to creep under the pressure that a
50   younger more active person might develop while involved in recreation or employment. The creep would cause the loss of the desired tolerance required between the plastic socket and the polished metal ball attached to the femur. These changes in dimensions disturb the distribution of walking forces which in turn accelerates more creep and wear. Eventually the increased pain requires a traumatic revision operation. One objective of this invention is to provide a process for making UHMWPE prosthetic joints with improved

creep resistance hence removing some of the age restriction existing with regard to the present polyethylene joints.

SUMMARY OF THE INVENTION

The object of this invention is to provide a process for making a tough UHMWLPE composition and articles that display a creep resistance, when exposed to a temperature of $23\pm1°C$ and a relative humidity of $50\mp2\%$ for 24 hours under a compression of 1000 psi, of less than 1% without sacrificing excellent tensile and flexural properties.

Specifically, the product obtained is a shaped UHMWLPE article exhibiting an elastic or flexural modulus of 250,000-500,000 psi, a tensile stress at yield of 3500-4500 psi, a tensile stress at break of 4000-9000 psi, a tensile modulus of 300,000-700,000 psi, an elongation of 200-500%, a notched Izod impact resistance of 12-20 ft. lb. per in. of notch, a creep at a compression of 1000 psi of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 1,000,000-10,000,000 (the molecular chain length between folds being greater than 3500Å), a single crystalline melting point of greater than 144°C (as measured by differential scanning calorimetry) the reduction in said melting point upon reheating being greater than 11°C above that of the starting polymer and an infrared crystallinity index of at least about 0.45.

The process for obtaining the shaped article of this invention involves six (6) important steps:

1. forming, by milling or casting or the like the article from UHMWLPE having a molecular weight of 400,000-10,000,000, preferably at least 1,000,000 and most preferably at least 6,000,000;

2. surrounding the article with an inert material that is collapsible and impermeable; and placing the surrounded article in a pressure vessel containing a gaseous fluid, preferably argon;

3. heating the vessel to a temperature of at least 190°C but no greater than 300°C, preferably 200°C-230°C, and raising the pressure in the vessel to at least 2800 atmospheres (ATM), preferably at least 3000 ATM;

4. maintaining the temperature and pressure substantially as selected in step 3 for at least 0.5 hour, preferably at least one hour;

5. thereafter, cooling by reducing the temperature to a temperature at least below about 160°C-170°C preferably to 160°C or below, most preferably below 140°C, while maintaining a pressure of at least 2800 ATM preferably at least 3000 ATM, at a slow rate, the rate of cooling being such that temperature gradients in the shaped article are substantially avoided. The polymer must be cooled slowly at the high pressure until it is fully crystallized. At 3000 ATM pressure, the crystallization temperature of UHMWLPE of over one million molecular weight is in the range of 170°C-190°C. The pressurized vessel should be cooled slowly to insure that the temperature of the polymer is not significantly above the vessel temperature, particularly if the pressure vessel construction does not permit means for measuring the temperature of the polymer itself; and

6. cooling and releasing the pressure on the shaped article in a manner such that any remelting of the article is prevented. This is accomplished by cooling at least to a temperature below the atmospheric pressure melting point, i.e., about 130°C-135°C preferably below 120°C, most preferably below 100°C and releasing the pressure to reduce it from at least 2800 ATM to approximately 1 ATM, either sequentially or simultaneously. It should be understood that it is necessary to cool the polymer to a temperature below its melting point at any particular pressure to insure that none of the polymer melts as the pressure is reduced since lowering the pressure lowers the melting point.

It has been found necessary to protect the surface of the article by enclosing it in a thin can during the process.

A very important step is the fifth step, i.e. cooling in a manner that limits severe temperature gradients in the article. For example, for a 1 inch X 6 inch rod, a cooling rate of approximately 10°C per hour is usually necessary. Cooling rates no greater than 10°C per hour are preferred. Whatever cooling rate is used, cooling requires careful control in order to limit temperature gradients during cooling. Cooling rapidly, as taught in the prior art, will not provide the desired article.

An additional step is expected to further improve the usefulness of the resulting product. A preliminary heat treatment is applied which subjects the UHMWPE to a temperature approaching, but not reaching, the decomposition point of the UHMWPE, preferably of between 320-340°C in an inert atmosphere for at least 0.5 hours.

This invention is particularly useful for manufacturing shaped articles where temperature gradients pose

a problem during the cooling step, i.e., where the article's cross-sectional dimensions are at least 1 inch x at least 1 inch, usually for joints at least 1 inch x at least 2 inches. Specifically, the importance of this step and of this invention is manifest in producing articles having as its smallest dimension 0.2 inch, i.e., at least 0.2 inch in thickness. It has been found that in such articles, the temperature gradients must still be

5   controlled by the process of this invention in order to obtain the desired product.

In addition to utility in the field of orthopedic replacement, the products are expected to prove useful in other applications also requiring the special properties of the products. Not only shaped articles are of interest, but also films and fibers as well as other "downstream" forms and unshaped granular forms of the products will prove useful. Film to be formed of the product of Example 1 is described in Example 6. These

10 examples are illustrative only, and other forms, shaped and unshaped, of the composition are contemplated within the scope of the invention. Therefore, "article" shall include both shaped articles and unshaped articles.

In the best mode known at this time for using the process of this invention, the gas used in the pressure vessel is argon. Specifically, the shaped article is formed from commercially available UHMWLPE. It is

15 necessary to protect the UHMWLPE from any entry of the gas into the polymer by surrounding the article completely with a thin stainless steel or similar metal can. It should be understood that other gaseous fluids may be used in place of argon. So long as the gas is not affected by the temperatures and pressures used in the process, the gas may be used. Such gases include, but are not lmited to, the noble gases, nitrogen, etc.

20 In the next step, the protected article is placed in an argon-filled pressure vessel and a pressure of at least 2000 ATM is applied with argon and the vessel is heated to about 220°C for about 6 hours. Thereafter, the temperature is "ramped" down at a rate no greater than about 10°C per hour to about 160°C while maintaining the pressure above 2800 ATM. The temperature is then "ramped" down at a maximum rate to 50°C while maintaining the high pressure, after which the pressure is released.

25 For purposes of this invention, ultrahigh molecular weight linear polyethylene (UHMWLPE) is defined as a linear polyethylene having an estimated weight-average molecular weight in excess of about 400,000, usually 1,000,000 to 10,000,000 as defined by a melt index (ASTMD-1238) of essentially zero and a reduced specific viscosity (RSV) greater than 8, preferably 25-30. The relationships of RSV to intrinsic viscosity and to molecular weight are those developed by R. Chaing as presented by P. S. Francis et al. in

30 J. Polymer Science, 31, 453 (1958).

The improved properties of the products of this process are reflected in a tensile modulus of at least 300 kpsi, a flex modulus of at least 250 kpsi, ultimate tensile strength greater than 4000 psi, yield strength greater than 3500 psi and an elongation at break no greater than 500%.

A very important property of the product is its creep resistance. For prosthetic devices, e.g. knee, hip,

35 elbow joints, etc., any substantial creep can be devastating in the loss of the benefits of extremely expensive surgery. Thus, the shaped articles resulting from this invention display as little as a 0.5% loss in thickness when subjected to a compression pressure of 1000 psi for 24 hours at a temperature of 23°C and a relative humidity of 50% in accordance with ASTM D-621.

Perhaps the most characteristic property of the product is its infrared crystallinity index (IRCI). This

40 property, which provides a reasonably accurate reflection of the crystallinity of this material, is in a range never before attained with any polyethylene materials. To determine this index, samples are first obtained by microforming thin sections. Heat and pressure should be avoided during preparation of the samples. IRCI is the ratio of the band at 1894 reciprocal centimeters (cm⁻¹) to the band at 1305 reciprocal centimeters (cm⁻¹). Since the band at 1894 cm⁻¹ is attributed to the crystalline nature of the material and

45 the band at 1305 cm⁻¹ is attributed to its amorphous nature, IRCI increases as the crystallinity increases. The product displays an IRCI of at least 0.45. In fact, values of 0.73 and higher have been obtained. On the other hand, IRCI values for prior known UHMWLPE's seldom reach above 0.3.

It should be appreciated that the step of forming the article by milling, casting, or the like from UHMWLPE may be performed as the first step in the process (i.e., before heating or preheating) or as the

50 last step in the process (i.e., after the cooling step).

The invention will be more clearly understood by referring to the drawing and example, which follow. In the drawing, Figure 1 is a schematic diagram of the equipment used in the process for forming the product of the invention using argon gas.

In the example, most of the properties are measured using standard ASTM tests. All of the physical

55 measurements were carried out under constant humidity (50% relative humidity) and temperature (23°C) conditions.

Tensile modulus, ultimate tensile strength, yield strength and elongation are measured according to ASTM D-638 with the following modifications:

* samples machined into shape without lubricating fluid
* type I tensile bar
* cross head speed = 0.2"/min for tensile modulus
2.0"/min for tensile stress and elongation.

Creep resistance is measured in accordance with ASTM D-621 with the following modifications:
* samples machined into cylinders without the use of lubricating fluids
* samples measured 0.5" x 0.5" x 0.5"

Flexural properties are measured according to ASTM D-790 with the following modifications:
* samples machined into shape without the use of lubricating fluids
* typical flex bar measures 0.125" thick x 0.5" width x 5" length
* span or gage is 2.0". (This was determined by a span/depth ratio of 16/l.)
* cross head speed = 0.05"/min (calculated based on span).

Impact resistance is measured using the notched Izod test given in ASTM D-256 with the following modifications:
* samples machined into shape without the use of lubricating fluid
* type A or notched IZOD
* specimen size is 0.5" x 2.5"
* 0.4" from bottom of vertex to opposite side
* 1.25" impacted end (from end of bar to vertex of notch)
* the notch should be the specified angle of 22.5 degrees.

The following non-limiting examples illustrate the basic principles and unique advantages of the present invention. Various changes and modifications may be made without departing from the spirit and scope of the present invention.

EXAMPLE 1

The material used in this example is American Hoechst 415 GUR ultrahigh molecular weight polyethylene. It was obtained in the form of bars, 3". in diameter and up to 5' long in length. The material will be referred to as UHMWLPE. The molecular weight was over 1,000,000.

One or more pieces of the UHMWLPE 11 were placed into stainless steel, seamless, 48" long cylinders or sleeves 12. The thickness of the stainless steel was 1/8". The bottom of the cylinders was closed by welding a stainless steel cap 13 onto the bottom of the cylinder. The top of the cylinder was partially closed by welding on a modified cap 14 which contained a vacuum port not shown. The cylinder was then evacuated using a vacuum pump and sealed by crimping the port to form a can that surrounds the piece of UHMWLPE completely. The sealed cylinder was then placed in a containment vessel 16 large enough to hold 15 cylinders. The containment vessel 16 was then placed into a hot isostatic pressing (HIP) unit 17 with molybdenum heating units 18. Thermocouples were added to monitor the temperature of the cylinders.

The basic function of the HIP process is to uniformly heat a load while applying pressure uniformly to all surfaces. The pressure medium used in this case was argon. The gas entered at 15 and exited at 19. The UHMWPE is protected from the argon by the stainless steel cans.

The process conditions were:
1. Apply pressure to 39,000 psi.
2. Heat to 220° C.
3. Hold for 6 hours at 220° C and a minimum pressure of 41,000 psi.
4. Ramp temperature down at a rate no faster than 10° C per hour to 160° C. Pressure is maintained above 41,000 psi during this time.
5. Ramp temperature down at maximum rate to 50° C while maintaining the pressure above 41,000 psi.
6. Below 50° C, pressure may be let down and the cycle ended.

The UHMWPE rods were then removed from the sleeves and parts were fabricated for physical testing. It is noted that the material produced exhibits much higher tensile modulus, flex modulus, melting point, density and creep resistance than the starting material (Control A).

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	DSC Melting Point	Density	
Material	(°C)	(grams/cc)	IRCI
Control	137.0-140.7°C	.93-.94	0.24
Example 1	148.0-152.0°C	.947	≥ 0.45

ASTM D638	Control A	Example 1
Flex Modulus kpsi	165	291
Tensile Modulus kpsi	185	315
Ultimate Tensile kpsi	4500	4688
ASTM D638		
Yield kpsi	3476	4082
Elongation (break) %	262	227
[values are averages of 5 tests]		
ASTM D621 Creep Test		
Load		
500 psi	.5	.3 % deformation
1000 psi	1.6	.7
2000 psi	5.9	2.4

Additional evidence of the products' distinctiveness is found in data produced by small angle X-ray testing. A truly characteristic small-angle X-ray scattering plot of desmeared intensity (by the method of P. W. Schmidt, Acta Cryst., 13, 480 (1960) and Acta Cryst., 19, 938 (1965)) (I x (2 theta) squared) versus scattering angle (2 theta) for the material of the invention exhibits two distinct scattering peaks associated with crystal long spacings in the range of 480 angstroms (at 2 theta = .184 degrees) and 4610 angstroms (at 2 theta = .0192 degrees). The presence of the sharp diffraction peak at the lower angle is indicative of an extended polymer chain conformation (with a lamellar thickness greater than 2000 angstroms) whereas the more diffuse higher-angle peak corresponds to a lamellar thickness characteristic of conventional folded chain PE. This provides clear evidence for the presence of two scattering peaks in the subject invention material which correspond to lamellar thicknesses both above and below 2000 angstroms. By comparison, the previously patented extended chain polyethylene of Lupton et al., was reported to exhibit a complete absence of any detectable small angle X-ray scattering in the range of 50 to 2000 angstroms. Consequently this work demonstrates that the subject invention material is morphologically distinguishable from Lupton et al.

EXAMPLE 2

The process described in Example 1 may be modified to yield a product with properties even more suitable for orthopedic replacements than the starting material. It is suggested that the UHMW polyethylene be preliminarily heated to a point closely approaching, but not reaching, the decomposition point of the UHMW polyethylene, preferably between 320-340°C, in an atmosphere of N2 or in a vacuum for six hours. Once so pre-heated, the article is otherwise to be treated as in Example 1.

It is expected that the addition of the preliminary heating step to the process will yield a product displaying improved tensile yield strength, improved elongation (%) at break, and lower creep resistance than the product of Example 1 or the starting material.

6

EXAMPLE 3

5 Effect of Sequence of Heat-Treatment, Cooling, Reheating to a Lower Temperature, and Pressure Recrystallization on UHMWPE.

The process described in Example 2 may also be modified to yield a product with properties superior to that found in the starting material. It is suggested that the UHMW polyethylene be preliminarily heated to

10 a point approaching, but not reaching, the decomposition point of the UHMW polyethylene, preferably between 320-340 °C, in an atmosphere of N_2 or in a vacuum for 5 hours. It is then reheated to approximately 225 °C, and pressure recrystallized as in Example 1.

It is expected that the described sequence of preliminary heat treatment, cooling, reheating to a lower temperature, and pressure recrystallization will yield a product displaying improved elongation (%) at break,

15 higher crystallinity index (IR), a higher IZOD impact value, and lower creep resistance than the starting material.

EXAMPLE 4

20

Effect of Preheating by Refluxing

25
The process described in Example 3 may be further modified to yield a product with properties superior to that of the starting material and with at least an improved elongation (%) at break as compared to the products yielded by other embodiments of the invention.

It is suggested that a rod approximately 3" x 18" of UHMWPE (e.g., Hoechst, Hostalen GUR 415) be

30 preliminarily heated in refluxing vapors of Krytox®-143AZ (E. I. du Pont de Nemours and Company, Wilmington, Delaware) at approximately 33-35 °C for more than 0.5 hours.

Krytox®-143AZ is a perfluoroalkylpolyether that is a non-flammable, chemically inert liquid having unusually high thermal and oxidative stability. Other materials demonstrating these characteristics may also be suitable. The refluxing system should be protected by a nitrogen or other inert atmosphere and wrapped

35 with glass insulation to facilitate slow, non-precipitous cooling.

It is expected that the described sequence of preliminary heat treatment by refluxing, cooling, reheating to a lower temperature, and pressure recrystallization will yield a product displaying improved elongation (%) at break, expected to be from 250-900, while retaining a high tensile strength at yield and a high tensile modulus.

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EXAMPLE 5

45 A 3" diameter bar (rod), 18" in length, of American Hoechst Hostalen GUR 415 ultrahigh molecular weight polyethylene, would be heated in an oven and then would be encapsulated with low molecular weight polyethylene by rolling the hot rod onto a 1/16" sheet of low molecular weight polyethylene heated to 180 °C on a large hot plate. An intervening sheet of "Teflon" Polytetrofluoroethylene film should be kept on the encapsulated rod to prevent sticking to the hot plate. The rod ends are similarly sealed. The "Teflon"

50 film should be kept on the encapsulated rod to prevent sticking in the reactor.

The bar should be heated to 225 °C under a nitrogen atmosphere and transfered to the reactor at 225 °C. After sealing, the reactor pressure is taken to 3000 atmospheres which should cause the temperature to reach 237 °C. The reactor should be permitted to cool to 180 °C in 6.5 h, then maintained at this temperature for 1h. The temperature is dropped to 170 °C, held at this temperature for 3h, then should

55 be cooled slowly to 150 °C from where it is cooled rapidly.

The rod, which remains coated, should be cut and machined into two test pieces (A and B) which should give results showing improved properties. For example, one would expect to find at 1st Heat a melting point, °C, in the range of 149 to 155 and a heat of fusion, J/g, in the range of 200.0 to 220.0. At

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2nd heat melting point, °C, is expected in the range of 130 to 140.0 with a heat of fusion, J/g, expected in the range of 140.0 to 146. At crystallinity index (IR) of approximately 0.57, the tensile strength of the material (psi) at yield is expected in the range of 4000 to 4500, at maximum is expected in the range of 7000 to 9000, and at break is expected in the range of 7000 to 9000. Elongation, % at break, is expected in the range of 320 to 350. Modulus, Kpsi, is expected in the range of 350 to 365.0. Creep Deformation, % measured by ASTM D621, is expected to be approximately 0.6 The IZOD Impact (ftlb/in. of notch) is expected to be in the range of 15.5 to 16.0.

EXAMPLE 6

A 5.75" segment of enhanced ultrahigh molecular weight polyethylene prepared as in Example 1, should be skived to two films (A and B), of 11 mil and 5 mil thickness, respectively. The following properties may be expected.

The tensile strength of the material (psi) at yield is expected to range from 3000 to 3200, at maximum is expected to range from 4000 to 7000, at break is expected to range from 4000 to 7000, and at 5% elongation is expected to be 2500 to 2800. The tensile modulus (kpsi) is expected to range from 125. 0 to 200. 0. The elongation at break (%) is expected to range from 200 to 500.

The skived films could be hot drawn in a tenter frame at 140°C. If one piece of the 5 mil film is drawn 6 fold in one direction the results could be tensile strength (psi) at yield that is approximately 37,820, at maximum that is approximately 42,100, at break that is approximately 46,400. Tensile modulus (Kpsi) could be approximately 93. Elongation at break (%) could be approximately 56 with a thickness in mils of 2.6.

If a second piece of the 5 mil film could be drawn 3 fold in both directions the results could be tensile strength (psi) at yield that is approximately 13,800, at maximum that is approximately 19,400, at break that is approximately 19,000. Tensile modulus (Kpsi) could be approximately 95.0. Elongation at break (%) could be approximately 132 with a thickness in mils of 1.6.

Claims

1. A process for obtaining a shaped article of an ultrahigh molecular weight linear polyethylene exhibiting a flexural modulus of 250,000-500,000 psi, a tensile stress at yield of 3500-4500 psi, a tensile stress at break of 4000-9000 psi, a tensile modulus of 300,000-700,000 psi, a notched Izod impact resistance of 12-25 ft. lb. per inch of notch, a creep at a compression of 1000 psi of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 1,000,000-10,000,000, a single crystalline melting point of greater than 144°C, the reduction in said melting point upon reheating being greater than 11°C and an infrared crystallinity index of at least about 0.45 consisting essentially of the following steps:

   (a) forming said article of an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000-10,000,000;

   (b) surrounding said article with an inert material that is collapsible and impermeable;

   (c) subjecting said surrounded article to a gas under pressure of at least 2800 ATM and a temperature of 190°C-300°C;

   (d) maintaining the temperature from 190°C-300°C and the pressure of at least 2800 ATM for at least 0.5 hour;

   (e) reducing the temperature to below 160°C-170°C, while maintaining the pressure at at least 2800 ATM, the rate of reduction in temperature being such that temperature gradients in the shaped article are substantially avoided; and

   (f) cooling to a temperature of about 130°C or below and releasing the pressure to approximately 1 ATM in a manner such that remelting of said article is prevented.

2. The process of Claim 1 subjecting said article before step (d) to a preliminary heat treatment at temperatures approaching, but less than, the decomposition point of the article, preferably between 320-340°C, in an inert atompshere for at least 0.5 hours.

3. The process of Claim 2 wherein said heat treatment before step (c) is accomplished by reflux vapors.

4. The process of Claim 1 wherein said article is enclosed within a stainless steel material that prevents said gas from contacting the surfaces of said article.

5. The process of Claim 4 wherein said gas is argon.
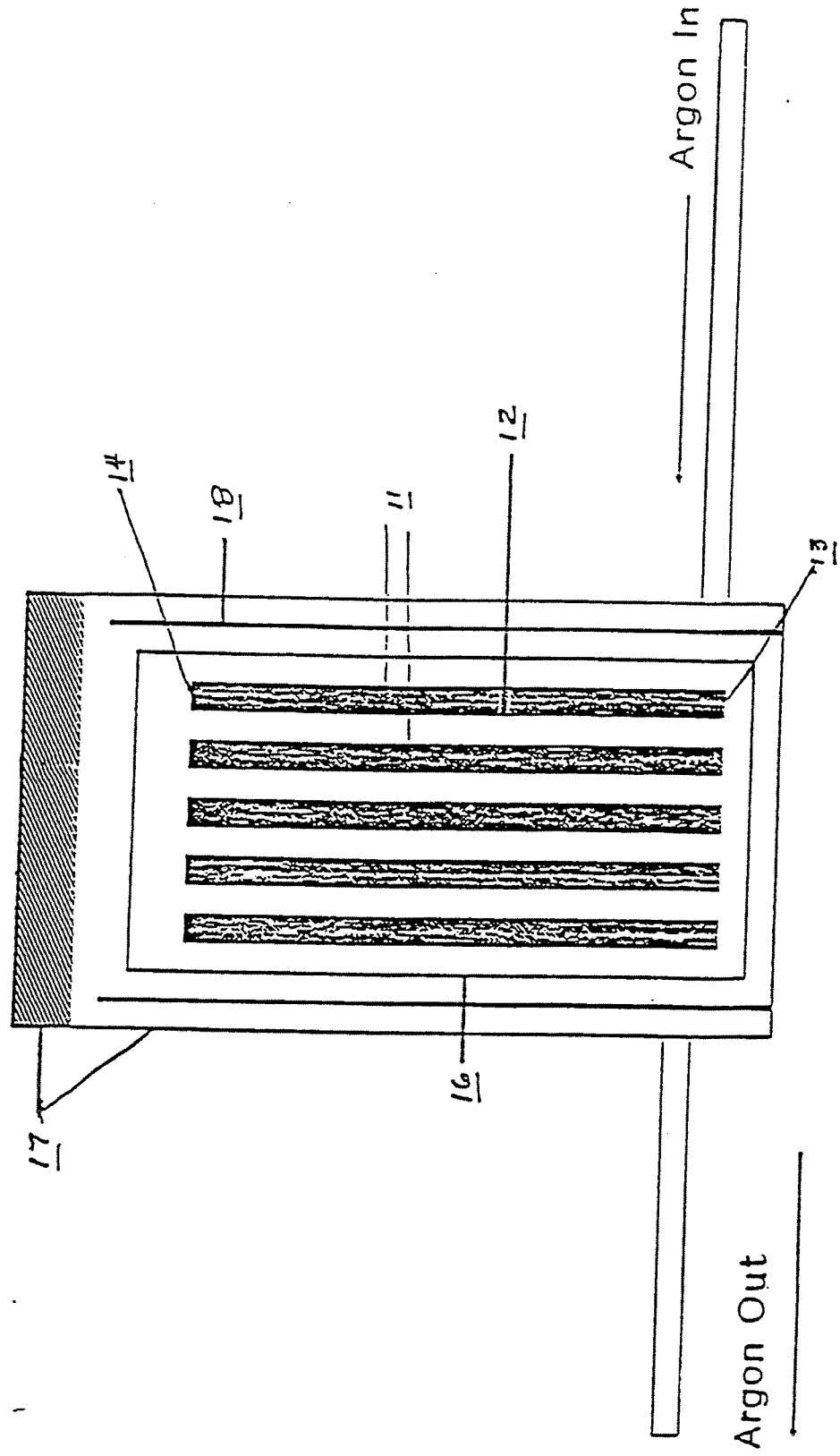
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6. The process of Claim 5 wherein said pressure in step (b) is at least 3000 ATM.

7. The process of Claim 5 wherein said temperature in step (c) is 190°C-230°C.

8. The process of Claim 5 wherein the temperature and pressure in step (f) is maintained for at least one hour.

9. The process of Claim 1 wherein step (a) is performed after step (f) is performed.

10. An ultrahigh molecular weight linear polyethylene exhibiting a flexural modulus of 250,000-500,000 psi, a tensile stress at yield of 3500-9000 psi, a tensile stress at break of 4000-9000 psi, a tensile modulus of 300,000-700,000 psi, a notched Izod impact resistance of 12-25 ft. lb. per inch of notch, a creep at a compression of 1000 psi of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 1,000,000-10,000,000, a single crystalline melting point of greater than 144°C, the reduction in said melting point upon reheating being greater than 11°C and an infrared crystallinity index of at least about 0.45 formed by the process consisting essentially of the following steps:

(a) forming said article of an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000-10,000,000;

(b) surrounding said article with an inert material that is collapsible and impermeable;

(c) subjecting said surrounded article to a gas under pressure of at least 2800 ATM and a temperature of 190°C-300°C;

(d) maintaining the temperature from 190°C-300°C and the pressure of at least 2800 ATM for at least 0.5 hour;

(e) reducing the temperature to below 160°C-170°C, while maintaining the pressure at at least 2800 ATM, the rate of reduction in temperature being such that temperature gradients in the shaped article are substantially avoided; and

(f) cooling to a temperature of about 130°C or below and releasing the pressure to approximately 1 ATM in a manner such that remelting of said article is prevented.

11. The product by the process of Claim 10 which is subjected before step (d) to a preliminary heat treatment at temperatures approaching, but less than, the decomposition point of the article, preferably between 320-340°C, in an inert atmosphere for at least 0.5 hours.

12. The product by the process of Claim 11 which is subjected to said heat treatment before step (c) by means of refluxing vapors.

13. The product by the process of Claim 10 which is enclosed within a stainless steel material that prevents said gas from contacting the surfaces of said article.

14. The product by process of Claim 13 which is produced with the use of argon.

15. The product by process of Claim 14 which is subjected in step (b) to pressure of at least 3000 ATM.

16. The product by process of Claim 14 which is subjected in step (c) to temperatures in the range of 190°C-230°C.

17. The product by process of Claim 14 which is subjected in step (f) to temperatures and pressures maintained for at least one hour.

18. The product by process of Claim 10 which is produced when step (a) is performed after step (f) is performed.

FIGURE 1

Argon In

Argon Out

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	POLYMER, vol. 22, January 1981, pages 23-28, IPC Business Press, London, GB; BHATEJA: "Uniaxial tensile creep behaviour of ultra high molecular weight linear polyethylene" * Page 28, conclusions *	1	A 61 L 27/00 A 61 F 2/32 C 08 L 23/06
A	JOURNAL OF POLYMER SCIENCE: PART A-2, POLYMER PHYSICS, vol. 7, 1969, pages 2051-2059, John Wiley & Sons, New York, US; DAVIDSON & WUNDERLICH: "Extended-chain crystals. II. Crystallization of polythelene under elevated pressure" * Page 2052, lines 32-38 *	1	

TECHNICAL FIELDS
SEARCHED (Int. Cl.5)

A 61 L
A 61 F
C 08 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29-03-1990	GOOVAERTS R.E.

(54) **Chemically crosslinked ultrahigh molecular weight polyethylene for artificial human joints**

Chemisch vernetztes ultrahochmolekulares Polyethylen für künstliche menschliche Gelenke

Polyéthylène de poids moléculaire ultra élevé chimiquement réticulé pour articulations humaines artificielles

• POLYMER, vol. 30, no. 5, May 1989, GB, pages 866-873, XP000569234 DIJKSTRA D.J. ET AL: "Cross-linking of ultra-high molecular weight polyethylene in the melt by means of electron beam irradiation"
• POLYMER, vol. 23, no. 09, August 1982, GB, pages 1944-1952, XP000569235 DE BOER J. ET AL: "Cross-linking of ultra-high molecular weight polyethylene in the melt by means..."
• DATABASE WPI Derwent Publications Ltd., London, GB; AN 87-338571[48] XP002001745 & JP-A-62 243 634 (NIPPON OIL KK) , 24 January 1987
• PATENT ABSTRACTS OF JAPAN vol. 009, no. 021 (C-263) & JP-A-59 168050 (MITSUBOSHI BELT KK), 21 September 1984,
• JOURNAL OF MACROMOLECULAR SCIENCE - PHYSICS, vol. B26, no. 1, 1987, US, pages 37-58, XP000569227 NARKIS M. ET AL: "Structure and tensile behavior of irradiation- and peroxide-crosslinked polyethylenes"
• PATENT ABSTRACTS OF JAPAN vol. 016, no. 501 (C-0996), 16 October 1992 & JP-A-04 185651 (FUJIKURA LTD.), 2 July 1992,
• JOURNAL OF APPLIED POLYMER SCIENCE, vol. 48, 1993, US, pages 711-719, XP002001744 QU B.J.: "Photocross-linking of low-density polyethylene. II. Structure and morphology"

Remarks:
The file contains technical information submitted after the application was filed and not included in this specification

Description

Technical Field Of The Invention

[0001]   The present invention relates to polymers. It discloses a method for enhancing the wear-resistance of polymers, especially polymers that are to be irradiated, by crosslinking the polymers. The crosslinked polymers may be annealed to stabilize their size shrinkage. The polymers disclosed herein are particularly useful for making in vivo implants.

Background Of The Invention

[0002]   Ultrahigh molecular weight polyethylene (hereinafter referred to as "UHMW polyethylene") is commonly used to make prosthetic joints such as artificial hip joints. In recent years, it has become increasingly apparent that tissue necrosis and interface osteolysis, in response to UHMW polyethylene wear debris, are primary contributors to the long-term loosening failure of prosthetic joints. For example, the process of wear of acetabular cups of UHMW polyethylene in artificial hip joints introduces many microscopic wear particles into the surrounding tissues. The reaction of the body to these particles includes inflammation and deterioration of the tissues, particularly the bone to which the prosthesis is anchored. Eventually, the prosthesis becomes painfully loose and must be revised. It is generally accepted by orthopaedic surgeons and biomaterials scientists that the reaction of tissue to wear debris is the chief cause of long-term failure of such prostheses.

[0003]   Laboratory experiments and examination of worn polyethylene components, as used in acetabular cups of total hip prostheses, after removal from patients, have shown that polyethylene wear in vivo primarily involves three fundamental mechanisms: adhesive, abrasive, and fatigue wear (Brown, K.J., et al., Plastics in Medicine & Surgery Plastics & Rubber Institute, London, 2.1-2.5 (1975); Nusbaum, H.J. & Rose, R.M., J. Biomed. Materials Res., 13: 557-576 (1979); Rostoker, W., et al., J. Biomed. Materials Res., 12:317-335 (1978); Swanson, S.A.V. & Freeman, M. A.R., Chapter 3, "Friction, lubrication and wear.", The Scientific Basis of Joint Replacement, Pittman Medical Publishing Co., Ltd. (1977).}

[0004]   Adhesive wear occurs when there is local bonding between asperities on the polymer and the opposing (metal or ceramic) counterface. If the ratio of the strength of the adhesive bond to the cohesive strength of the polymer is great enough, the polymer may be pulled into a fibril, finally breaking loose to form a wear particle. Small wear particles (measuring microns or less) are typically produced.

[0005]   Abrasive wear occurs when asperities on the surface of the femoral ball, or entrapped third-body particles, penetrate into the softer polyethylene and cut or plow along the surface during sliding. Debris may be immediately formed by a cutting process, or material may be pushed to the side of the track by plastic deformation, but remain an integral part of the surface.

[0006]   Fatigue wear is dependent on cyclic stresses applied to the polymer. As used herein, fatigue wear is an independent wear mechanism involving crack formation and propagation within the polymer. Cracks may form at the surface and coalesce, releasing wear particles as large as several millimeters and leaving behind a corresponding pit on the surface, or cracks may form a distance below the surface and travel parallel to it, eventually causing sloughing off of large parts of the surface.

[0007]   There are gaps in the prior art regarding the contributions of the above three basic mechanisms to the wear of polyethylene cups in vivo. While numerous laboratory studies and analyses of retrieved implants have provided valuable details on wear in vivo, there is ongoing disagreement regarding which wear mechanisms predominate and what are the controlling factors for wear.

[0008]   However, it is clear that improving the wear resistance of the UHMW polyethylene socket and, thereby, reducing the amount of wear debris generated each year, would extend the useful life of artificial joints and permit them to be used successfully in younger patients. Consequently, numerous modifications in physical properties of UHMW polyethylene have been proposed to improve its wear resistance.

[0009]   UHMW polyethylene components are known to undergo a spontaneous, post-fabrication increase in crystallinity and changes in other physical properties. {Grood, E.S., et al., J. Biomedical Materials Res., 16:399-405 (1976); Kurth, J., et al., Trans. Third World Biomaterials Congress, 589 (1988); Rimnac, C.M., et al., J. Bone & Joint Surgery, 76-A-(7):1052-1056 (1994)}. These occur even in stored (non-implanted) cups after sterilization with gamma radiation which initiates an ongoing process of chain scission, crosslinking, and oxidation or peroxidation involving free radical formation. {Eyerer, P. & Ke, Y.C., J. Biomed. Materials Res., 18:1137-1151 (1984); Nusbaum, H. J. & Rose, R.M., J. Biomed. Materials Res., 13:557-576 (1979); Roe, R.J., et al., J. Biomed. Materials Res., 15:209-230 (1981); Shen, C. & Dumbleton, J.H., Wear, 30:349-364 (1974)}. These degradative changes may be accelerated by oxidative attack from the joint fluid and cyclic stresses applied during use. {Eyerer, P. & Ke, Y.C., J. Biomed. Materials Res., supra; Grood, E.S., et al., J. Biomed. Materials Res., supra; Rimnac, C.M., et al., ASTM Symposium on Biomaterials' Me-

chanical Properties, Pittsburgh, May 5-6 (1992)).

[0010] On the other hand, it has been reported that the best total hip prosthesis for withstanding wear is one with an alumina head and an irradiated UHMW polyethylene socket, as compared to a un-irradiated socket. The irradiated socket had been irradiated with 10^8 rad of γ-radiation, or about 40 times the usual sterilization dose. {Oonishi, H., et al., Radiat. Phys. Chem., 39(6):495-504 (1992)}. The usual average sterilization dose ranges from 2.5 to 4.0 Mrad. Other investigators did not find any significant reduction in the wear rates of UHMW polyethylene acetabular cups which had been irradiated, in the solid phase, in special atmospheres to reduce oxidation and encourage crosslinking. (Ferris, B.D., J. Exp. Path., 71:367-373 (1990); Kurth, M., et al., Trans. Third World Biomaterials Congress, 589 (1988); Roe, R.J., et al., J. Biomed. Materials Res., 15:209-230 (1981); Rose, et al., J. Bone & Joint Surcrery, 62A(4):537-549 (1980); Streicher, R.M., Plastics & Rubber Processing & Applications, 10:221-229 (1988)}.

[0011] Meanwhile, DePuy.DuPont Orthopaedics has fabricated acetabular cups from conventionally extruded bar stock that has previously been subjected to heating and hydrostatic pressure that reduces fusion defects and increases the crystallinity, density, stiffness, hardness, yield strength, and resistance to creep, oxidation and fatigue. {U.S. Patent No. 5,037,928, to Li, et al., Aug. 6, 1991; Huang, D. D. & Li, S., Trans. 38th Ann. Mtg., Orthop. Res. Soc., 17:403 (1992); Li, S. & Howard, E. G., Trans. 16th Ann. Society for Biomaterials Meeting, Charleston, S.C., 190 (1990).} Silane cross-linked UHMW polyethylene (XLP) has also been used to make acetabular cups for total hip replacements in goats. In this case, the number of in vivo debris particles appeared to be greater for XLP than conventional UHMW polyethylene cup implants (Ferris, B. D., J. Exp. Path., 71:367-373 (1990)).

[0012] Other modifications of UHMW polyethylene have included: **(a)** reinforcement with carbon fibers {"Poly Two Carbon-Polyethylene Composite-A Carbon Fiber Reinforced Molded Ultra-High Molecular Weight Polyethylene", Technical Report, Zimmer (a Bristol-Myers Squibb Company), Warsaw (1977)}; and **(b)** post processing treatments such as solid phase compression molding {Eyerer, P., Polyethylene, Concise Encyclopedia of Medical & Dental Implant Materials, Pergamon Press, Oxford, 271-280 (1990); Li, S., et al., Trans. 16th Annual Society for Biomaterials Meeting, Charleston, S.C., 190 (1990); Seedhom, B.B., et al., Wear, 24:35-51 (1973); Zachariades, A.E., Trans. Fourth World Biomaterials Congress, 623 (1992)}. However, to date, none of these modifications has been demonstrated to provide a significant reduction in the wear rates of acetabular cups. Indeed, carbon fiber reinforced polyethylene and a heat-pressed polyethylene have shown relatively poor wear resistance when used as the tibial components of total knee prosthesis. (Bartel, D.L., et al., J. Bone & Joint Surgery, 68-A(7):1041-1051 (1986); Conelly, G.M., et al., J. Orthop. Res., 2:119-125 (1984); Wright, T.M., et al., J. Biomed. Materials Res., 15: 719-730 (1981); Bloebaum, R.D., et al., Clin. Orthop., 269:120-127 (1991); Goodman, S. & Lidgren, L., Acta Orthop. Scand., 63(3) 358-364 (1992); Landy, M. M. & Walker, P.S., J. Arthroplasty, Supplement, 3:S73-S85 (1988); Rimnac, C.M., et al., Trans. Orthopaedic Research Society, 17:330 (1992); Rimnac, C.M. et al., "Chemical and mechanical degradation of UHMW polyethylene: Preliminary report of an in vitro investigation," ASTM Symposium on Biomaterials' Mechanical Properties, Pittsburgh, May 5-6 (1992)}.

Summary Of The Invention

[0013] One aspect of the invention presents a method for reducing the crystallinity of a polymer so that it can better withstand wear. An effective method for reducing the crystallinity of the polymer is by crosslinking. For reduction of crystallinity, the polymer may be irradiated in the melt or, preferably, chemically crosslinked in the molten state. The method is particularly useful for polymer which undergoes irradiation sterilization in the solid state. It is advantageous if the crosslinked polymer is annealed to stabilize its shrinkage.

[0014] Another aspect of the invention presents a method for making in vivo implants based on the above treatment of the polymer.

[0015] Another aspect of the invention presents a polymer, made from the above method, having an increased ability to withstand wear.

[0016] Another aspect of the invention presents in vivo implants made from the polymer described above.

[0017] The implants of the present invention are in accordance with claim 1 or 3.

[0018] The implantable bearing components of the present invention are in accordance with claim 19 or 21. Methods of making an implant or improving its wear resistance are in accordance with any one of claims 32,33,42,43,52 and 53.

Brief Description Of The Drawings

[0019] FIG. 1 presents SEM micrographs of fracture surfaces of the compression molded UHMW polyethylene (after irradiation) at magnifications of (A) x 200 and (B) x 5000.

[0020] FIG. 2 presents SEM micrographs of fracture surfaces of compression molded UHMW polyethylene crosslinked with 1 wt% peroxide (after irradiation) at magnifications of (A) x 200 and (B) x 5000.

[0021] FIG. 3 presents the geometry of the acetabular cup tested for wear on the hip joint simulator used in EXAMPLE

2 below.

[0022] FIG. 4 presents a schamatic diagram of the hip joint simulator used in EXAMPLE 2 below.

[0023] FIG. 5 presents a graph comparing the amounts of wear of the modified and unmodified UHMW polyethylene cups during a run lasting a million cycles.

Detailed Description Of The Invention

[0024] Abbreviations used in this application are as follows:

DSC -- differential scanning calorimetry.
FTIR -- Fourier Transform Infrared Spectroscopy
SEM -- scanning electron microscopy
UHMW -- ultra-high molecular weight
UHMWPE -- ultra-high molecular weight polyethylene, also referred to as UHMW polyethylene
WAXS -- wide angle X-ray scattering

[0025] Cutting through the plethora of choices and confusion in the art, applicants discovered that a low degree of crystallinity is a major factor in increasing the ability of polyethylene to withstand wear in vivo, contrary to the above teaching of DePuy.DuPont Orthopaedics. Solid polymers that can crystallize generally contain both crystalline and amorphous states. These two states have different physical properties. The applicants believe that the crystalline component of polymers is more brittle and less wear-resistant than the amorphous component, the amorphous component being more ductile and more wear-resistant.

[0026] In the present invention, the degree of crystallinity of the polymer is preferably reduced by crosslinking. The crosslinking can be achieved by various methods known in the art, for example, by irradiation crosslinking of the molten polymer; photocrosslinking of the molten polymer; and crosslinking of the polymer with a free radical generating chemical. The preferred method is chemical crosslinking. As indicated, if the crosslinking is to be achieved by irradiation, the polymer should be irradiated in the melt, unlike the above mentioned prior art irradiation methods, such as in Oonishi et al. Applicants also discovered that such a crosslinked polymer is useful for in vivo implant because it is wear resistant. Such in vivo implant has not been envisioned by the prior art. Moreover, since acetabular cups are routinely sterilized by irradiation which increases the crystallinity of UHMW polyethylene {Bhateja, S.K., J. Macromol. Sci. Phys., B22:159 (1983); Bhateja, S.K., et al., J. Polym. Sci., Polym. Phys. Ed., 21:523 (1983); and Bhateja, S.K. & Andrews, E.H., J. Mater. Sci., 20:2839 (1985)}, applicants realized that the irradiation in fact makes the polymer more susceptible to wear, contrary to the teaching of the prior art such as Oonishi et al, supra. By crosslinking the polymer before sterilization by irradiation, applicants' method mitigates the deleterious effects of irradiation, such as chain scission. Applicants' method calls for determination of the crystallinity after irradiation to adjust the crosslinking conditions to reduce crystallinity. The polymer may also be irradiated under certain conditions e.g., in nitrogen atmosphere to reduce the immediate and subsequent amounts of oxidation. Reducing oxidation increases the amount of crosslinking. In producing acetabular cups, applicants discovered that both uncrosslinked and crosslinked cups show shrinkage in size, but crosslinked cups tend to shrink more than uncrosslinked cups. Thus, the present invention also provides for annealing the crosslinked polymer in order to shrink it to a stable size before reshaping the polymer.

[0027] Most importantly, implants which are produced by the foregoing methods of the invention are more wear resistant than conventional untreated polymer. Thus, an example of the present invention presents an UHMW polyethylene acetabular cup of a total hip prosthesis which has been chemically crosslinked by a peroxide, and then sterilized by irradiation, showing only one fifth of the wear of a control cup after a simulated year of in vivo use.

Method for Treating the Polymers

[0028] One aspect of the invention presents a method for treating a polymer to reduce its crystallinity to less than 45% to enable the resulting polymer to better withstand wear. The polymer's crystallinity is preferably reduced by crosslinking in the molten state followed by cooling to the solid state. Preferably, the crosslinking reduces the crystallinity of the polymer by about 10% to 50%; more preferably, by about 10% to 40%; and most preferably, by about 10% to 30% compared to an uncrosslinked polymer. For example, the preferable degree of crystallinity of crosslinked UHMW polyethylene is between about 24% to 44%; more preferably, between 29% to 44%; and most preferably, between about 34% to 44%. After sterilization by irradiation, the crosslinked polymer has a reduced crystallinity compared to the uncrosslinked polymer. Preferably, the irradiated crosslinked polymer possesses about 10% to 50%; more preferably, about 10% to 40%; and most preferably, about 10% to 30% less degree of crystallinity compared to the uncrosslinked but irradiated polymer. For example, the preferable degree of crystallinity of irradiated, crosslinked UHMW polyethylene is between about 28% to 51%; more preferably, between about 33% to 51%; and most preferably, between

about 39% to 51%. For example, EXAMPLE 1, Table 1 below shows the degree of crystallinity for UHMW polyethylene containing different weight percentage of peroxide. In the following EXAMPLE 2, UHMW polyethylene which was crosslinked by 1% weight (wt) peroxide exhibited about 39.8% crystallinity, i.e. about a 19% reduction in crystallinity compared to uncrosslinked UHMW polyethylene which possessed about 49.2% crystallinity. After gamma irradiation to an average dose of about 3.4 Mrad, the crosslinked UHMW polyethylene exhibits about 42% crystallinity, i.e., a reduction of about 25% in crystallinity compared to the originally uncrosslinked but radiation sterilized UHMW polyethylene which possessed about 55.8% crystallinity. Thus, it is contemplated that after the usual sterilization dosage in the solid state, which generally averages between 2.5 to 4.0 Mrad, the treated polymer preferably possesses less than about 45% crystallinity, and more preferably about 42% crystallinity or less. Also, the treated polymer preferably possesses less than about 43%, more preferably less than about 40%, crystallinity before irradiation in the solid state.

[0029] If the polymer is to be molded, e.g. as an acetabular cup, the polymer may be placed in the mold and crosslinked therein. Further crosslinking examples are: **(1)** irradiation of the polymer when it is in a molten state, e.g. UHMW polyethylene has been crosslinked in the melt by electron beam irradiation; and molten linear polyethylene has been irradiated with fast electrons (Dijkstra, D.J. et al., Polymer, 30:866-709 (1989); Gielenz G. & Jungnickle, B.J., Colloid & Polymer Sci., 260:742-753 (1982)}; the polymer may also be gamma-irradiated in the melt; and **(2)** photocrosslinking of the polymer in the melt, e.g. polyethylene and low-density polyethylene have been photocrosslinked {Chen, Y.L. & Ranby, B., J. Polymer Sci.: Part A: Polymer Chemistry, 27:4051-4075, 4077-4086 (1989)}; Qu, B.J. & Ranby, B., J. Applied Polymer Sci., 48:711-719 (1993)}.

Choices of Polymers

[0030] The polymers are generally polyhydrocarbons. Ductile polymers that wear well are preferred. Examples of such polymers include: polyethylene, polypropylene, polyester and polycarbonates. For example, UHMW polymers may be used, such as UHMW polyethylene and UHMW polypropylene. An UHMW polymer is a polymer having a molecular weight (MW) of at least about a million.

[0031] For in vivo implants, the preferred polymers are those that are wear resistant and have exceptional chemical resistance. UHMW polyethylene is the most preferred polymer as it is known for these properties and is currently widely used to make acetabular cups for total hip prostheses. Examples of UHMW polyethylene are: Hostalen GUR 415 medical grade UHMW polyethylene flake (Hoechst-Celanese Corporation, League City, Texas), with a weight average molecular weight of 6×10^6 MW; Hostalen GUR 412 with a weight average molecular weight of between 2.5×10^6 to 3×10^6 MW; Hostalen GUR 413 of 3×10^6 to 4×10^6 MW; RCH 1000 (Hoechst-Celanese Corp.); and HiFax 1900 of 4×10^6 MW (HiMont, Elkton, Maryland). GUR 412, 413 and 415 are in the form of powder. RCH 1000 is usually available as compression molded bars. Historically, companies which make implants have used GUR 412 and GUR 415 for making acetabular cups. Recently, Hoechst-Celanese Corp. changed the designation of GUR 415 to 4150 resin and indicated that 4150 HP was for use in medical implants.

Methods for Characterizing the Polymers (Especially the Determination of Their Crystallinity)

[0032] The degree of crystallinity of the crosslinked polymer may be determined after it has been crosslinked or molded. In case the treated polymer is further irradiated, e.g., to sterilize the polymer before its implant into humans, the degree of crystallinity may be determined after irradiation, since irradiation effects further crystallization of the polymer.

[0033] The degree of crystallinity can be determined using methods known in the art, e.g. by differential scanning calorimetry (DSC), which is generally used to assess the crystallinity and melting behavior of a polymer. Wang, X. & Salovey, R., J. App. Polymer Sci., 34: 593-599 (1987).

[0034] X-ray scattering from the resulting polymer can also be used to further confirm the degree of crystallinity of the polymer, e.g. as described in Spruiell, J.E., & Clark, E.S.,in "Methods of Experimental Physics", L. Marton & C. Marton, Eds., Vol. 16, Part B, Academic Press, New York (1980). Swelling is generally used to characterize crosslink distributions in polymers, the procedure is described in Ding, Z. Y., et al., J. Polymer Sci., Polymer Chem., 29: 1035-38 (1990). Another method for determining the degree of crystallinity of the resulting polymer may include FTIR {Painter, P.C. et al., "The Theory Of Vibrational Spectroscopy And Its Application To Polymeric Materials", John Wiley and Sons, New York, U.S.A. (1982)} and electron diffraction. FTIR assesses the depth profiles of oxidation as well as other chemical changes such as unsaturation {Nagy, E.V., & Li, S., "A Fourier transform infrared technique for the evaluation of polyethylene orthopaedic bearing materials", Trans. Soc. for Biomaterials, 13:109 (1990); Shinde, A. & Salovey, R., J. Polymer Sci., Polym. Phys. Ed., 23:1681-1689 (1985)}. A further method for determining the degree of crystallinity of the resulting polymer may include density measurement according to ASTM D1505-68.

Methods for Chemically Crosslinking the Polymers

[0035] The polymer is preferably chemically crosslinked to decrease its crystallinity. Preferably, the crosslinking chemical, i.e. a free radical generating chemical, has a long half-life at the molding temperature of the chosen polymer. The molding temperature is the temperature at which the polymer is molded. The molding temperature is generally at or above the melting temperature of polymer. If the crosslinking chemical has a long half-life at the molding temperature, it will decompose slowly, and the resulting free radicals can diffuse in the polymer to form a homogeneous crosslinked network at the molding temperature. Thus, the molding temperature is also preferably high enough to allow the flow of the polymer to occur to distribute or diffuse the crosslinking chemical and the resulting free radicals to form the homogeneous network. For UHMW polyethylene, the molding temperature is between 150° to 220°C and the molding time is between 1 to 3 hours; the preferable molding temperature and time being 170°C and 2 hours, respectively.

[0036] Thus, the crosslinking chemical may be any chemical that decomposes at the molding temperature to form highly reactive intermediates, free radicals, which would react with the polymers to form the crosslinked network. Examples of free radical generating chemicals are peroxides, peresters, azo compounds, disulfides, dimethacrylates, tetrazenes, and divinyl benzene. Examples of azo compounds are: azobis-isobutyronitride, azobisisobutyronitrile, and dimethylazodi isobutyrate. Examples of peresters are t-butyl peracetate and t-butyl perbenzoate.

[0037] Preferably the polymer is crosslinked by treating it with an organic peroxide. The preferable peroxides are 2,5-dimethyl-2,5-bis(tert-butylperoxy)-3-hexyne (Lupersol 130, Atochem Inc., Philadelphia, Pennsylvania); 2,5-dimethyl-2,5-di-(t-butylperoxy)-hexane; t-butyl α-cumyl peroxide; di-butyl peroxide; t-butyl hydroperoxide; benzoyl peroxide; dichlorobenzoyl peroxide; dicumyl peroxide; di-tertiary butyl peroxide; 2,5 dimethyl-2,5 di(peroxy benzoate) hexyne-3; 1,3-bis(t-butyl peroxy isopropyl) benzene; lauroyl peroxide; di-t-amyl peroxide; 1,1-di-(t-butylperoxy) cyclohexane; 2,2-di-(t-butylperoxy)butane; and 2,2-di-(t-amylperoxy) propane. The more preferred peroxide is 2,5-dimethyl-2,5-bis (tert-butylperoxy)-3-hexyne. The preferred peroxides have a half-life of between 2 minutes to 1 hour; and more preferably, the half-life is between 5 minutes to 50 minutes at the molding temperature.

[0038] Generally, between 0.2 to 5.0 wt% of peroxide is used; more preferably, the range is between 0.5 to 3.0 wt% of peroxide; and most preferably, the range is between 0.6 to 2 wt%.

[0039] The peroxide can be dissolved in an inert solvent before being added to the polymer powder. The inert solvent preferably evaporates before the polymer is molded. Examples of such inert solvents are alcohol and acetone.

[0040] For convenience, the reaction between the polymer and the crosslinking chemical, such as peroxide, can generally be carried out at molding pressures. Generally, the reactants are incubated at molding temperature, between 1 to 3 hours, and more preferably, for about 2 hours.

[0041] The reaction mixture is preferably slowly heated to achieve the molding temperature. After the incubation period, the crosslinked polymer is preferably slowly cooled down to room temperature. For example, the polymer may be left at room temperature and allowed to cool on its own. Slow cooling allows the formation of a stable crystalline structure.

[0042] The reaction parameters for crosslinking polymers with peroxide, and the choices of peroxides, can be determined by one skilled in the art. For example, a wide variety of peroxides are available for reaction with polyolefins, and investigations of their relative efficiencies have been reported {Lem, K.W. & Han, C.D., J. Appl. Polym. Sci., 27: 1367 (1982); Kampouris, E.M. & Andreopoulos, A.G., J. Appl. Polym. Sci., 34:1209 (1987) and Bremner, T. & Rudin, A. J. Appl. Polym. Sci., 49:785 (1993)}. Differences in decomposition rates are perhaps the main factor in selecting a particular peroxide for an intended application {Bremner, T. & Rudin, A. J. Appl. Polym. Sci., 49:785 (1993)}. Bremner and Rudin, id., compared three dialkyl peroxides on the basis of their ability to increase the gel content, crosslinking efficiency, and storage modulus of virgin polyethylene through a crosslinking mechanism and found that they decreased in the order of α,α-bis(tertiary butylperoxy)-p-diisopropyl benzene > dicumyl peroxide > 2,5-dimethyl-2,5-di-(tertiary butylperoxy)-hexyne-3 at the same active peroxide radical concentrations and temperature.

[0043] More specifically, peroxide crosslinking of UHMW polyethylene has also been reported {de Boer, J. & Pennings, A.J., Makromol. Chem. Rapid Commun., 2:749 (1981); de Boer, J. & Pennings, A.J., Polymer, 23:1944 (1982); de Boer, J., et al., Polymer, 25:513 (1984) and Narkis, M., et al., J. Macromol. Sci. Phys., B 26:37, 58 (1987)}. de Boer et al. crosslinked UHMW polyethylene in the melt at 180°C by means of 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexyne-3 and found that crosslinks and entanglements, whether trapped or not, contributed to the same degree to the decrease in crystallinity of UHMW polyethylene upon crosslinking (de Boer, J. & Pennings, A.J., Polymer, 23:1944 (1982)). It was concluded that an almost completely crosslinked (or gelled) material with high crystallinity and good mechanical properties could be obtained by using as little as 0.2-0.3 wt% of peroxide.

[0044] Some of the above references investigated the effect of peroxide crosslinking on UHMW polyethylene, such as in lowering crystallinity; and the effects of reaction parameters, such as peroxide concentrations {de Boer, J. & Pennings, A.J., Polymer, 23:1944 (1982); Narkis, M., et al., J. Macromol. Sci. Phys., B 26:37-58 (1987)}. However, these references do not address the effect of peroxide crosslinking or the lowering of crystallinity in relation to the wear property of the resulting polymer. For example, de Boer and Pennings, in Polymer, 23:1944 (1982), were concerned

with the effect of crosslinking on the crystallization behavior and the tensile properties of UHMW polyethylene. The authors found that tensile properties, such as tensile strength at break point and Young's modulus, of the UHMW polyethylene, showed a tendency to decrease with increasing peroxide content.

[0045]   Similarly, Narkis, M., et al., J. Macromol. Sci. Phys., B 26:37-58 (1987), separately determined the effects of irradiation and peroxide on the crosslinking and degree of crystallinity of UHMW polyethylene (Hostalen GUR 412), high molecular weight polyethylene, and normal molecular weight polyethylene. However, M. Narkis et al., did not study the inter-relationship of peroxide crosslinking and irradiation, nor their effects on wear resistance.

Use of Crosslinked Polymers for In Vivo Implants

[0046]   Another aspect of the invention presents a process for making in vivo implants using the above chemically crosslinked polymer. Since in vivo implants are often irradiated to sterilize them before implant, the present invention provides the further step of selecting for implant use, a polymer with about 45% crystallinity or less after irradiation sterilization. For γ-irradiation sterilization, the minimum dosage is generally 2.5 Mrad. The sterilization dosage generally falls between 2.5 and 4.0 Mrad. The preferable degree of crystallinity is between 25% to 45% crystallinity. In EXAMPLE 2 below, the polymer has about 39.8% crystallinity after crosslinking; and about 42% crystallinity after further irradiation with γ-radiation to an average dose of about 3.4 Mrad. Thus, the chemically crosslinked UHMW polymer preferably possesses less than about 43% crystallinity before irradiation in the solid state, and less than about 45% crystallinity after irradiation with γ-radiation to an average dose of about 3.4 Mrad.

Annealing of Crosslinked Polymers

[0047]   Applicants observed that both crosslinked and uncrosslinked polymers tended to shrink, but the crosslinked polymer tended to shrink more than the uncrosslinked polymer (see EXAMPLE 3 below). Thus, the present invention further provides for annealing a polymer to pre-shrink it to a size which will not shrink further (i.e. stabilize the polymer's shrinkage or size). Thus, one aspect of the invention provides for a method of: 1) crosslinking a polymer, 2) selecting a crosslinked polymer of reduced crystallinity, 3) annealing the polymer to stabilize its size. Thus, the polymer can be molded at a size larger than desired, and the molded polymer is then annealed to stabilize its size. After size stabilization, the molded polymer is then resized, such as by machining, into a product with the desired dimension.

[0048]   The annealing temperature is preferably chosen to avoid thermal oxidation of the crosslinked polymer which will increase its crystallinity. Thus, the annealing temperature is preferably below the melting point of the molded polymer before irradiation. For example, the melting temperatures of molded UHMW polyethylene and molded 1 wt% peroxide UHMW polyethylene are 132.6°C and 122.3°C, before irradiation, respectively. The preferable annealing temperature for both these molded UHMW polyethylenes is between 60°C to 120°C, before irradiation, and more preferably 100°C. These temperatures were determined by observation, based on experiments, of their minimal effect on thermal oxidation of the molded polymers. The annealing time is generally between 1 to 6 hours, and more preferably between 2 to 4 hours. In the case of UHMW polyethylene, the annealing time is preferably between 2 to 4 hours, and more preferably about 2 hours.

[0049]   To further avoid thermal oxidation of the crosslinked polymer, the annealing is most preferably conducted in a vacuum oven.

[0050]   To ensure that the crosslinked and annealed polymer has the desired degree of crystallinity, its degree of crystallinity is preferably determined after the annealing process, using the method(s) described previously.

Wear-Resistant Polymers

[0051]   Another aspect of the invention presents a polymer with 45% of crystallinity or less, in particular, after irradiation in the solid state and/or annealing. In EXAMPLE 2 below, the polymer has about 39.8% crystallinity after crosslinking; and about 42% crystallinity, after further irradiation with γ-radiation to an average dose of about 3.4 Mrad; or about 40.8% crystallinity, after crosslinking and annealing, but before irradiation in the solid state.

[0052]   The polymers of the present invention can be used in any situation where a polymer, especially UHMW polyethylene, is called for, but especially in situations where high wear resistance is desired and irradiation of the solid polymer is called for. More particularly, these polymers are useful for making in vivo implants.

In Vivo Implants Made of Crosslinked Polymers

[0053]   An important aspect of this invention presents in vivo implants that are made with the above polymers or according to the method presented herein. These implants are more wear resistant than their untreated counterpart, especially after irradiation. In particular, these in vivo implants are chemically crosslinked UHMW polymers, which have

been molded, annealed, and resized into the shape of the implants. Further, the chemically crosslinked UHMW polymer preferably possesses less than about 43% crystallinity before irradiation in the solid state, and less than about 45% crystallinity, after γ-irradiation to an average dose of 3.4 Mrad, in the solid state. The modified polymer can be used to make in vivo implants for various parts of the body, such as components of a joint in the body. For example, in the hip joints, the modified polymer can be used to make the acetabular cup, or the insert or liner of the cup, or trunnion bearings (e.g. between the modular head and the stem). In the knee joint, the modified polymer can be used to make the tibial plateau (femoro-tibial articulation), the patellar button (patello-femoral articulation), and trunnion or other bearing components, depending on the design of the artificial knee joint. In the ankle joint, the modified polymer can be used to make the talar surface (tibio-talar articulation) and other bearing components. In the elbow joint, the modified polymer can be used to make the radio-humeral joint, ulno-humeral joint, and other bearing components. In the shoulder joint, the modified polymer can be used to make the glenoro-humeral articulation, and other bearing components. In the spine, the modified polymer can be used to make intervertebral disk replacement and facet joint replacement. The modified polymer can also be made into temporo-mandibular joint (jaw) and finger joints. The above are by way of example, and are not meant to be limiting.

[0054]   Having described what the applicants believe their invention to be, the following examples are presented to illustrate the invention, and are not to be construed as limiting the scope of the invention.

EXAMPLES

EXAMPLE 1

Experimental Details

[0055]   Commercial-grade UHMW polyethylene GUR 415 (from Hoechst-Celanese Corporation, League City, Texas), with a weight average molecular weight of 6×10^6, was used as received. The peroxide used was 2,5-dimethyl-2,5-bis (tert-butylperoxy)-3-hexyne (Lupersol 130, Atochem Inc., Philadelphia, Pennsylvania). The reason for choosing Lupersol 130 was its long half-life at elevated temperature. The peroxide will decompose slowly, and the resultant free radicals can diffuse in the specimen to form a homogeneous network at elevated temperatures.

[0056]   Mixing of the UHMW polyethylene and the peroxide was accomplished by dispersing polyethylene powder in an acetone solution of the peroxide and subsequently evaporating the solvent (de Boer, J., et al., J. Polym. Sci., Polym. Phys. Ed., 14:187 (1976); de Boer, J. & Pennings, A.J., Makromol. Chem, Rapid Commun., 2:749 (1981) and de Boer, J. & Pennings, A.J., Polymer, 23:1944 (1982)). The mixed powder (22g) was poured into the mold cavity and then compression molded in a mold between two stainless-steel plates at 120°C and ram pressure 11×10^3 kPa for 10 minutes in order to evacuate the trapped air in the powder. After pressing, the pressure was reduced to 7.5×10^3 kPa and the specimen was heated to 170°C by circulated heating oil. These conditions were held for 2 hours. The half-life time of peroxide at 170°C in dodecane is about 9 minutes. After 2 hours, pressure was increased to 15×10^3 kPa to avoid cavities in the specimen and sink marks on the surface and the specimen was slowly cooled in the mold to room temperature. The mold was in the shape of an acetabular cup for a total hip prosthesis.

[0057]   The specimens were irradiated with γ-rays at room temperature in air atmosphere by SteriGenics International (Tustin, California). Cobalt-60 was used as a source of gamma irradiation. The radiation doses were delivered at a dose rate of 5 kGy/hr. Specimens received doses to an average of about 34 kGy (i.e., an average of about 3.4 Mrad).

[0058]   The physical properties of specimens before and after irradiation were characterized by DSC, equilibrium swelling, FTIR, and WAXS measurements. Surface morphology was examined by SEM.

Results and Discussion

[0059]   Before irradiation, the degree of crystallinity, peak melting temperature, and recrystallization temperature for the peroxide-free specimen are 49.2%, 132.6 and 115.5°C, respectively. For a 1 wt% peroxide specimen, the degree of crystallinity, peak melting temperature, and recrystallization temperature are reduced to 39.8%, 122.3 and 110.1°C, respectively. Peroxide crosslinking reactions are accompanied by the decomposition of peroxide and abstraction of hydrogen atoms, and the resulting combination of alkyl radicals to produce carbon-carbon crosslinks. Generally, this reaction was performed above the melting temperature of the polymer. Thus the crosslinking step preceded the crystallization step. It was suggested that crystallization from a crosslinked melt produced an imperfect crystal, and crosslinks suppressed crystal growth, resulting in the depression of melting temperature and a decreased crystallinity (decreased crystallite size) {de Boer, J. et al., J. Polym. Sci., Polym. Phys. Ed., 14:187 (1976); de Boer, J. & Pennings, A.J., Makromol. Chem, Rapid Commun., 2:749 (1981); de Boer, J. & Pennings, A.J., Polymer, 23:1944 (1982) and Narkis, M., et al., J. Macromol. Sci. Phvs., B26:37 (1987)}. Wide-angle x-ray scattering shows that the degree of crystallinity, crystal perfection and size decrease after peroxide crosslinking. For swelling measurement, the peroxide-free

specimen dissolves completely in boiling p-xylene. The gel content, degree of swelling, and average molecular weight between crosslinks for the 1 wt% peroxide specimen are 99.6%, 2.53, and 1322 (g/mol), respectively. Because of the extremely long polymer chains in UHMW polyethylene, only a few crosslinks were needed for gelation. In addition, an almost 100% gel can be obtained by peroxide crosslinking because no chain scission occurs by peroxide crosslinking.

[0060] After irradiation, the degree of crystallinity and peak melting temperature for the peroxide-free specimen were increased to 55.8% and 135°C, respectively. It was suggested that irradiation-induced scission of taut tie molecules permits recrystallization of broken chains from the noncrystalline regions, and results in an increase in the degree of crystallinity and an increased perfection of existing folded chain crystallites (Narkis, M., et al., J. Macromol. Sci. Phys., B26:37 (1987); Bhateja, S.K., J. Macromol. Sci. Phys., B22:159 (1983); Bhateja, S.K., et al., J. Polym. Sci., Polym. Phys. Ed., 21:523 (1983); Kamel, I. & Finegold, L., J. Polym. Sci., Polym. Phys. Ed., 23:2407 (1985); Shinde, A. & Salovey, R., J. Polym. Sci., Polym, Phys. Ed., 23:1681 (1985); Bhateja, S.K. & Andrews, E.H., J. Mater. Sci., 20:2839 (1985); Minkova, L., Colloid Polym. Sci., 266:6 (1988); Minkova, L. & Mihailov, M., Colloid Polym. Sci., 268:1018 (1990) and Zhao, Y., et al., J. Appl. Polym. Sci., 50:1797 (1993)}. The gel content after irradiation for the peroxide-free specimen was 70.8%.

[0061] For the 1 wt% peroxide specimen, the degree of crystallinity and peak melting temperature after irradiation were increased to 42% (about 2% increase) and 125.1°C, respectively. The gel content decreased to 97.5% after irradiation, whereas, the degree of swelling and molecular weight between crosslinks increased to 3.35 and 2782 (g/mol), respectively. Apparently, irradiation-induced scission of taut tie molecules resulted in a decreased gel content and an increased degree of swelling. However, after peroxide crosslinking, the effect of irradiation on network properties was mitigated. As a result of peroxide crosslinking, radiation-induced chain scission becomes less important in determining gel content. We suggest that peroxide crosslinking reduces the effect of irradiation on the crosslinked network because crosslinks introduced by peroxide crosslinking stabilize chain fragments resulting from the scission of taut tie molecules and suppress recrystallization of broken chains. Wide-angle x-ray scattering showed that crystal perfection increased after irradiation. It is suggested that crystal perfection was improved by irradiation-induced scission of taut tie molecules in the amorphous regions.

[0062] FTIR measurements showed that, after irradiation, the carbonyl concentration significantly increased. This is because the free radicals produced by irradiation reacted with oxygen dissolved and/or diffused in the polymer. In addition, the carbonyl concentration in irradiated peroxide-crosslinked samples was higher, compared to the peroxide-free sample (after irradiation). Peroxide crosslinking produces tertiary carbons, therefore, the concentration of tertiary carbons increases with increasing peroxide concentration. Applicants believe that tertiary carbons are more susceptible to oxidation during irradiation. Therefore, carbonyl concentration in the irradiated peroxide-crosslinked samples increased with increasing peroxide concentration.

[0063] After irradiation, scanning electron micrographs were taken of the fracture surfaces of the peroxide-free and 1 wt% peroxide specimens, compression molded at 170°C for 2 hours and subsequently slowly cooled to room temperature. The micrographs are shown in Figs. 1 and 2, respectively. As shown in Fig. 1, a brittle (rough) fracture boundary of size comparable to that of the original UHMW polyethylene powder particles is observed. Close examination (x 5000 magnification) shows an oriented nodular structure, composed of many smooth, submicron spheres. These smooth, minute spheres are believed to correspond to those present in the raw UHMW polyethylene powder and to form an aggregate. In Fig. 2, peroxide crosslinked samples show a ductile (smooth) fracture surface, compared to the rough fracture surface of peroxide-free specimen. The difference in appearance of fracture surfaces for peroxide-free and 1 wt% peroxide specimens is due to the crystallinity difference. After irradiation, the degree of crystallinity for the peroxide-free and 1 wt% peroxide specimens were 55.8 and 42%, respectively. It is believed that the peroxide-free specimen (55.8% crystallinity) suffered higher forces and less deformation during the fracturing process, leading to a sharp break in the polymer.

[0064] The crosslinking experiment was also conducted with different concentrations of Lupersol 130, using a smaller amount, 5 g, of GUR 415 and a smaller mold which was in the form of a disk. It was observed that the degree of crystallinity of the crosslinked polymer decreased with increased concentrations of Lupersol 130. The result is shown in Table 1 below:

TABLE 1

wt% Peroxide	Crystallinity (%) Before Irradiation	Crystallinity (%) After Irradiation
0	49.2	55.8
0.2	44.0	50.0
0.4	41.6	46.8
0.6	41.3	46.2

TABLE 1 (continued)

wt% Peroxide	Crystallinity (%) Before Irradiation	Crystallinity (%) After Irradiation
0.8	40.0	45.0
1.0	39.8	42.0
1.5	36.8	36.8
2.0	36.5	36.7

Conclusions

[0065] Peroxide crosslinking leads to a decrease in the degree of crystallinity, peak melting temperatures, and re-crystallization temperatures for 1 wt% peroxide specimen. Irradiation produces crosslinking in amorphous regions plus extensive scission of taut tie molecules and leads to increased crystallinity and crystal perfection, reduces gel content, and increases the degree of swelling of a crosslinked network.

[0066] Peroxide crosslinking reduces the effect of irradiation on the crosslinked network. This is because crosslinks introduced by peroxide crosslinking can stabilize the chain fragments resulting from the scission of taut tie molecules and suppress recrystallization of broken chains.

[0067] FTIR measurements showed that, after irradiation, the carbonyl concentration significantly increased. This is because the free radicals produced by irradiation react with oxygen dissolved and/or diffused in the polymer. In addition, carbonyl concentration in the irradiated peroxide-crosslinked samples is higher, compared to the peroxide-free sample (after irradiation). This is because peroxide crosslinking introduces tertiary carbons which are more susceptible to oxidation during irradiation, so that the carbonyl concentration in the irradiated peroxide-crosslinked samples increases.

[0068] Wide-angle x-ray scattering shows that crystal perfection increases after irradiation. It is suggested that crystal perfection is improved by irradiation-induced scission of taut tie molecules in the amorphous regions.

[0069] The peroxide-free specimen shows brittle fracture because of higher crystallinity (55.8%), whereas, the 1 wt% peroxide specimen shows ductile fracture due to lower crystallinity (42%).

EXAMPLE 2

Materials and Methods

[0070] In this example, the wear resistance of the polyethylenes treated (modified) and untreated (unmodified) with peroxide in EXAMPLE 1 were tested. The control (unmodified) and modified polyethylenes were compression molded directly into the form of acetabular cups. These were then exposed to an average of approximately 3.4 Mrad of gamma radiation (SteriGenics International, Tustin, California), to simulate the condition of cups that would be used in patients. Due to different amounts of post-molding shrinkage, the internal surface of each cup was machined to provide nearly identical internal diameters and ball-to-cup clearances among the control and modified cups (Fig. 3). As shown in Fig. 3B, the cup's outer radius **1** is 24.5 mm, its inner radius **2** is 16.1 mm, its height **3** is 29.8 mm, and its diameter **4** is 49.0 mm

[0071] The cups were pre-soaked in distilled water for three weeks prior to the wear test to minimize fluid absorption during the wear test. The wear cups were mounted on the hip joint simulator, including four cups of control polyethylene and three cups of modified polyethylene. Each cup was held in a urethane mold and mounted in a stainless steel test chamber, with a plexiglass wall to contain the bovine serum lubricant. The lubricant had 0.2% sodium azide added to retard bacterial degradation, and 20 milli-Molar ethylene-diaminetetraacetic acid (EDTA) to prevent precipitation of calcium phosphate on the surfaces of the ball (McKellop, H. & Lu, B., " Friction and Wear of Polyethylene-Metal and Polyethylene-Ceramic Hip Prostheses on a Joint Simulator, Fourth World Biomaterials Congress, Berlin, Apr. 1992, 118). A polyethylene skirt covered each chamber to minimize air-borne contamination. The cups were oscillated against highly polished femoral balls of cast cobalt-chromium alloy, as used on artificial hips. The simulator applied a Paul-type cyclic load at one cycle per second {Paul, J.P., Proc. Instn. Mech. Engrs., 181, Part 3J, 8-15, (1967)} with a 2000N peak, simulating the load on the human hip during normal walking, and the cups were oscillated through a bi-axial 46 degree arc at 68 cycles per minute. At intervals of 250,000 cycles, the cups were removed from the wear machine, rinsed, inspected and replaced with fresh lubricant. At 500,000 cycles and one million cycles, all of the cups were removed from the wear simulator, cleaned, dried and weighed to determine the weight loss due to wear. One million cycles is the equivalent of about one year's use of a prosthetic hip in a patient. Fig. 4 presents a schematic diagram of the hip joint simulator. The arrow indicates the direction of the computer controlled simulated physiological load exerted on the simulated hip joint. The simulator contains: a torque transducer **5,** the acetabular cup **6,** a dual axis

offset drive block **7**, a test chamber **8**, serum **9**, and a femoral head **10**.

[0072] Three soak-correction acetabular cups of each material (control and modified) were prepared in an identical manner, but were not wear tested. These cups were mounted in a separate test frame and a cyclic load, identical to that used in the wear test, was applied. These soak-correction cups were cleaned and weighed together with the wear test cups, and the average weight <u>gain</u> of the correction cups was added to the apparent weight <u>loss</u> of the wear test cups (<u>i.e.</u> to correct for fluid absorption by the wear test cups that would obscure the weight loss due to wear).

Results and Discussion

[0073] Because of the apparent "negative" wear at 0.5 million cycles (discussed below), the wear <u>rates</u> were calculated and compared for all of the cups only for the interval from 0.5 to 1.0 million cycles. The four control polyethylene cups showed comparable amounts of wear (Fig. 5), with an average corrected wear rate of 19.19 (S.D.=2.38) milligrams per million cycles (Table 2). This was within the range that applicants have measured for cups of conventional UHMW polyethylene in a variety of studies that applicants have run.

[0074] The wear was much lower for the modified cups (Fig. 5). As shown in Table 2, the mean wear rate for the modified cups was 4.12 (S.D.=1.26) milligrams per million cycles, <u>i.e.</u> about one-fifth of the wear of the control cups. This difference was statistically significant at the level of $p=0.0002$).

TABLE 2

WEAR RATES FOR CONTROL AND MODIFIED POLYETHYLENES (INTERVAL FROM 0.5 TO 1.0 MILLION CYCLES)			
MATERIAL	CUP NUMBER	WEAR RATE (mg/million cycles)	MEAN WEAR RATE (STANDARD DEVIATION)
CONTROL POLYETHYLENE	C2	21.67	19.19 (2.38)
	C3	16.78	
	C4	17.57	
	C9	20.76	
MODIFIED POLYETHYLENE	M4	4.08	4.12 (1.26)
	M5	2.88	
	M7	5.39	

[0075] For the data point at 0.5 million cycles, the corrected weights were <u>lower</u> than the weights before the wear test. This was most likely the result of the wear being very small, and the fluid absorption by the test cups being slightly greater than the average gain of the soak correction cups, such that the correction factor did not entirely offset the fluid gain by the wear cups (giving an apparent "negative" wear). A small difference in water absorption rates between the wear cups and the correction cups could arise due to differences in equilibrium temperatures (the wear cups were typically at 35°C to 45°C, whereas the soak correction cups were at room temperature, about 20°C), due to mechanical agitation of the serum during oscillation of the wear test chambers, or other causes.

EXAMPLE 3

[0076] During the wear test in the simulator described in EXAMPLE 2, it was discovered that the acetabular cups shrunk at simulated human body temperature. In order to stabilize the shrinkage, in this experiment (unrelated to EXAMPLE 2), the cups were annealed at 100°C in a vacuum oven for 2 hours. After annealing, the total shrinkage in diameter for uncrosslinked and crosslinked cups was approximately 1% and 2%, respectively. The degrees of crystallinity of the annealed cups were determined by DSC. The degree of crystallinity of the uncrosslinked polymer was unchanged, whereas that of the crosslinked polymer was increased by approximately 1%. To test for further shrinkage, the cups were again put in the vacuum oven at 80°C for two hours, and no further shrinkage was observed.

[0077] The present invention has been described with reference to specific embodiments. However, this application is intended to cover those changes and substitutions which may be made by those skilled in the art without departing from the scope of the appended claims.

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Claims

1. An implant for use within a body, said implant being made of irradiated crosslinked ultrahigh molecular weight polyethylene having a polymeric structure of between 28% and 51% crystallinity as measured by DSC, so as to increase the wear resistance of said implant within the body.

2. The implant of claim 1, wherein the implant is further sterilised, the crystallinity being as measured after the sterilisation.

3. An implant for use within a body, said implant being made of a crosslinked ultrahigh molecular weight polyethylene having a polymeric structure of less than 45% crystallinity as measured by DSC, so as to increase the wear resistance of said implant within the body.

4. The implant of claim 3, wherein said ultrahigh molecular weight polyethylene has between 24% to 44% crystallinity as measured by DSC.

5. The implant of claim 3 or 4, wherein the implant is further sterilised.

6. The implant of claim 5, wherein the crystallinity is as measured after sterilisation.

7. The implant of claim 2 or 5, wherein said sterilisation is by means of irradiation.

8. The implant of any preceding claim, wherein said crosslinked ultrahigh molecular weight polyethylene is further **characterized by** (a) having been crosslinked with a peroxide concentration of 1 wt% and having a polymeric structure of 99.6% or almost 100% gel content, or (b) having been crosslinked with a peroxide concentration of 1 wt% followed by irradiation and having a polymeric structure of 97.5% gel content.

9. The implant of any preceding claim, wherein the crosslink is achieved according to the method selected from the group consisting of: chemically crosslinking a polyethylene, irradiation crosslinking a polyethylene in a molten state, and photocrosslinking a polyethylene in a molten state.

10. The implant of claim 7, wherein said implant is irradiated in the solid state.

11. The implant of claim 10, wherein said implant is irradiated in air with gamma-radiation at a dose of 34kGy.

12. The implant of any preceding claim, wherein said crosslinked ultrahigh molecular weight polyethylene is further **characterized by** having been annealed so as to shrink it to a stable size.

13. The implant of any preceding claim, wherein said crosslinked ultrahigh molecular weight polyethylene is further **characterized by** a polymeric structure of 3.35 degree of swelling provided by crosslinking with a peroxide concentration of 1wt% followed by irradiation, or a polymeric structure of 2.53 degree of swelling by crosslinking with a peroxide concentration of 1 wt%.

14. The implant of any preceding claim, wherein the implant is a component for use in a joint prosthesis.

15. The implant of claim 14, wherein the component is a bearing component.

16. The implant of claim 14 or 15, wherein the joint prosthesis is selected from the group consisting of: hip, knee, ankle, elbow, jaw, shoulder, finger joint prostheses and spine facet joint prostheses.

17. The implant of claim 16, wherein the joint prosthesis is selected from the group consisting of hip and knee joint prostheses.

18. The implant of claim 17, wherein the implant is selected from the group consisting of: an acetabular cup, an insert of an acetabular cup, and a liner of an acetabular cup.

19. An implantable bearing component with improved wear resistance, said implantable component comprising an irradiated crosslinked ultrahigh molecular weight polyethylene having increased wear resistance, and a polymeric

structure **characterized by** 28% to 51% crystallinity as measured by DSC.

20. The implantable bearing component of claim 19, wherein the component is further sterilised, the crystallinity being as measured after the sterilisation

21. An implantable bearing component with improved wear resistance, said implantable component comprising a crosslinked ultrahigh molecular weight polyethylene having increased wear resistance, said crosslinked ultrahigh, molecular weight polyethylene having a polymeric structure **characterized by** less than 45% crystallinity as measured by DSC.

22. The implantable bearing component of claim 21, wherein the crosslinked ultrahigh molecular weight polyethylene has a polymeric structure **characterized by** between 24% to 44% crystallinity as measured by DSC.

23. The implantable bearing component of claim 21 or 22, wherein the component is further sterilised.

24. The implantable bearing component of claim 23, wherein said crystallinity is as measured after sterilisation.

25. The implantable bearing component of claim 20 or 24, wherein said sterilisation is by means of irradiation.

26. The implantable bearing component of any one of claims 19 to 25, wherein the crosslinked ultrahigh molecular weight polyethylene has a polymeric structure **characterized by** a 3.35 degree of swelling provided by crosslinking with a peroxide concentration of 1 wt% followed by irradiation, or a polymeric structure of 2.53 degree of swelling by crosslinking with a peroxide concentration of 1wt%.

27. The implantable bearing component of any one of claims 19 to 26, wherein the crosslinked ultrahigh molecular weight polyethylene is further **characterized by** (a) having been crosslinked with a peroxide concentration of 1 wt% and having a polymeric structure of 99.6% or almost 100% gel content, or (b) having been crosslinked with a peroxide concentration of 1 wt% followed by irradiation and having a polymeric structure of 97.5% gel content.

28. The implantable bearing component of any one of claims 19 to 27, wherein the crosslink is achieved according to the method selected from the group consisting of: chemically crosslinking a polyethylene, irradiation crosslinking a polyethylene in a molten state, and photocrosslinking a polyethylene in a molten state.

29. The implantable bearing component of any one of claims 19 to 28, wherein the implantable bearing component is used in a joint prosthesis.

30. The implantable bearing component of claim 29, wherein the joint prosthesis is selected from the group consisting of: hip and knee joint prostheses.

31. The implantable bearing component of claim 30, wherein the implantable bearing component is selected from the group consisting of: an acetabular cup, an insert of an acetabular cup, and a liner of an acetabular cup.

32. A method of producing an implant with improved wear resistance, comprising the steps of: crosslinking a polyethylene to produce an irradiated crosslinked ultrahigh molecular weight polyethylene having a polymeric structure **characterized by** 28% to 51 % crystallinity as measured by DSC, and annealing the crosslinked ultrahigh molecular weight polyethylene to preshrink and stabilize its size before making it into an implant.

33. A method of producing an implant with improved wear resistance, comprising the steps of: crosslinking a polyethylene to produce a crosslinked ultrahigh molecular weight polyethylene having a polymeric structure **characterized by** less than 45% crystallinity as measured by DSC, and annealing the crosslinked ultrahigh molecular weight polyethylene to preshrink and stabilize its size before making it into an implant.

34. The method of claim 33, wherein the polymeric structure is **characterized by** between 24% to 44% crystallinity as measured by DSC.

35. The method of any one of claims 32 to 34 including a sterilisation step, wherein the crystallinity is as measured after the sterilisation step.

36. The method as claimed in claim 35, wherein the sterilisation step is achieved by means of irradiation.

37. The method of any one of claims 32 to 36, wherein the polymeric structure is **characterized by** a 3.35 degree of swelling provided by crosslinking with a peroxide concentration of 1wt% and irradiation, or a 2.53 degree of swelling by crosslinking with a peroxide concentration of 1 wt%.

38. The method of any one of claims 32 to 37, wherein said crosslinked ultrahigh molecular weight polyethylene is further **characterized by** (a) having been crosslinked with a peroxide concentration of 1 wt% and having a polymeric structure of 99.6% or almost 100% gel content, or (b) having been crosslinked with a peroxide concentration of 1 wt% followed by irradiation and having a polymeric structure of 97.5% gel content.

39. The method of any one of claims 32 to 38, wherein the implant is a component for use in a joint prosthesis.

40. The method of any one of claims 32 to 39, wherein the implant is a bearing component.

41. The method of any one of claims 32 to 40, wherein the implant is selected from the group consisting of: an acetabular cup, an insert of an acetabular cup, and a liner of an acetabular cup.

42. A method for improving the wear resistance of an implant for use within a body, said implant being made from irradiated crosslinked ultrahigh molecular weight polyethylene, said method comprising the step of crosslinking a polyethylene to provide a polymeric structure of between 28% to 51% crystallinity as measured by DSC.

43. A method for improving the wear resistance of an implant for use within a body, said implant being made from ultrahigh molecular weight polyethylene, said method comprising the step of crosslinking a polyethylene to provide a polymeric structure with less than 45% crystallinity as measured by DSC.

44. The method of claim 43, wherein the polymeric structure is **characterized by** between 24% to 44% crystallinity as measured by DSC.

45. The method of any one of claims 42 to 44, further comprising the step of sterilising the implant, wherein the crystallinity is as measured after the sterilisation.

46. The method of claim 45, wherein the sterilisation is by means of irradiation.

47. The method of any one of claims 42 to 46, wherein the polymeric structure is **characterized by** a 3.35 degree of swelling provided by crosslinking with a peroxide concentration of 1wt% and irradiation, or a 2.53 degree of swelling by crosslinking with a peroxide concentration of 1wt%.

48. The method of any one of claims 42 to 47, wherein said crosslinked ultrahigh molecular weight polyethylene is further **characterized by** (a) having been crosslinked with a peroxide concentration of 1 wt% and having a polymeric structure of 99.6% or almost 100% gel content, or (b) having been crosslinked with a peroxide concentration of 1 wt% followed by irradiation and having a polymeric structure of 97.5% gel content.

49. The method of any one of claims 42 to 48, wherein the implant is a component for use in a joint prosthesis.

50. The method of any one of the claims 42 to 49, wherein the implant is a prosthetic bearing component.

51. The method of any one of the claims 42 to 50, wherein the implant is selected from the group consisting of: an acetabular cup, an insert of an acetabular cup, and a liner of an acetabular cup.

52. A method for making and improving wear resistance of an implant for use within a body, comprising the steps of: (a) crosslinking a polyethylene to provide an irradiated crosslinked ultrahigh molecular weight polyethylene with a polymeric structure of between 28% to 51% crystallinity as measured by DSC, and (b) forming the implant from said crosslinked ultrahigh molecular weight polyethylene.

53. A method for making and improving wear resistance of an implant for use within a body, comprising the steps of: (a) crosslinking a polyethylene to provide a crosslinked ultrahigh molecular weight polyethylene with a polymeric structure of less than 45% crystallinity as measured by DSC, and (b) forming the implant from said crosslinked

ultrahigh molecular weight polyethylene.

54. The method of claim 53, wherein the polymeric structure is **characterized by** between 24% to 44% crystallinity as measured by DSC.

55. The method of any one of claims 52 to 54, wherein the step of crosslinking further provides the crosslinked ultrahigh molecular weight polyethylene with a polymeric structure of 3.35 degree of swelling provided by crosslinking with a peroxide concentration of 1 wt% and irradiation, or a 2.53 degree of swelling provided by crosslinking with a peroxide concentration of 1wt%.

56. The method of any one of claims 52 to 55, wherein the step of crosslinking is (a) by crosslinking with a peroxide concentration of 1 wt% and further provides the ultrahigh molecular weight polyethylene with a polymeric structure of 99.6% or almost 100% gel content, or (b) by crosslinking with a peroxide coacentration of 1 wt% followed by irradiation and further provides the ultrahigh molecular weight polyethylene with a polymeric structure of 97.5% gel content.

57. The method of any one of claims 52 to 56, wherein the implant is a component for use in a joint prosthesis.

58. The method of any one of the claims 52 to 57, wherein the implant is a prosthetic bearing component.

59. The method of any one of the claims 52 to 58, wherein the implant is selected from the group consisting of: an acetabular cup, an insert of an acetabular cup, and a liner of an acetabular cup.

60. The method of any one of the claims 52 to 59, further comprising the step of annealing the crosslinked ultrahigh molecular weight polyethylene at a temperature of 60°C to 120°C for 1 to 6 hours to stabilize its size.

Patentansprüche

1. Implantat zur Verwendung innerhalb eines Körpers, wobei das Implantat aus bestrahltem vernetzten ultrahochmolekularen Polyethylen mit einer polymeren Struktur von zwischen 28% und 51% Kristallinität, wie gemessen durch DSC, hergestellt ist, um die Verschleißbeständigkeit des Implantats innerhalb des Körpers zu verstärken.

2. Implantat nach Anspruch 1, wobei das Implantat weiterhin sterilisiert wird, wobei die Kristallinität wie nach der Sterilisation gemessen ist.

3. Implantat zur Verwendung innerhalb eines Körpers, wobei das Implantat aus einem vernetzten ultrahochmolekularen Polyethylen mit einer polymeren Struktur von weniger als 45% Kristallinität, wie gemessen durch DSC, hergestellt ist, um die Verschleißbeständigkeit des Implantats innerhalb des Körpers zu verstärken.

4. Implantat nach Anspruch 3, wobei das ultrahochmolekulare Polyethylen zwischen 24% und 44% Kristallinität, wie gemessen durch DSC, hat.

5. Implantat nach Anspruch 3 oder 4, wobei das Implantat weiterhin sterilisiert wird.

6. Implantat nach Anspruch 5, wobei die Kristallinität wie nach der Sterilisation gemessen ist.

7. Implantat nach Anspruch 2 oder 5, wobei die Sterilisation mittels Bestrahlung erfolgt.

8. Implantat nach einem vorhergehenden Anspruch, wobei das vernetzte ultrahochmolekulare Polyethylen weiter **dadurch gekennzeichnet ist, daß** es (a) mit einer Peroxidkonzentration von 1 Gew.-% vernetzt worden ist und eine polymere Struktur von 99,6% oder fast 100% Gelgehalt aufweist oder (b) mit einer Peroxidkonzentration von 1 Gew.-% und nachfolgender Bestrahlung vernetzt worden ist und eine polymere Struktur von 97,5% Gelgehalt aufweist.

9. Implantat nach einem vorhergehenden Anspruch, wobei die Vernetzung nach dem Verfahren, ausgewählt aus der Gruppe, bestehend aus: chemischer Vernetzung eines Polyethylens, Strahlenvernetzung eines Polyethylens in einem geschmolzenen Zustand und Photovernetzung eines Polyethylens in einem geschmolzenen Zustand, er-

reicht wird.

10. Implantat nach Anspruch 7, wobei das Implantat im festen Zustand bestrahlt wird.

11. Implantat nach Anspruch 10, wobei das Implantat in Luft mit Gamma-Bestrahlung mit einer Dosis von 34 kGy bestrahlt wird.

12. Implantat nach einem vorhergehenden Anspruch, wobei das vernetzte ultrahochmolekulare Polyethylen weiter **dadurch gekennzeichnet ist, daß** es getempert worden ist, um zu einer stabilen Größe zu schrumpfen.

13. Implantat nach einem vorhergehenden Anspruch, wobei das vernetzte ultrahochmolekulare Polyethylen weiter durch eine polymere Struktur mit einem Quellungsgrad von 3,35, bereitgestellt durch Vernetzen mit einer Peroxid- konzentration von 1 Gew.-% und nachfolgender Bestrahlung, oder eine polymere Struktur mit einem Quellungsgrad von 2,53 durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% **gekennzeichnet** ist.

14. Implantat nach einem vorhergehenden Anspruch, wobei das Implantat eine Komponente zur Verwendung in einer Gelenkprothese ist.

15. Implantat nach Anspruch 14, wobei die Komponente eine Lagerkomponente ist.

16. Implantat nach Anspruch 14 oder 15, wobei die Gelenkprothese aus der Gruppe, bestehend aus: Hüft-, Knie-, Knöchel-, Ellenbogen-, Kiefer-, Schulter-, Fingergelenkprothesen und Wirbelsäulengelenkflächenprothesen, aus- gewählt ist.

17. Implantat nach Anspruch 16, wobei die Gelenkprothese aus der Gruppe, bestehend aus: Hüft- und Kniegelenk- prothesen, ausgewählt ist.

18. Implantat nach Anspruch 17, wobei das Implantat aus der Gruppe, bestehend aus: einer Hüftgelenkspfanne, einem Einsatz einer Hüftgelenkspfanne und einer Einlage einer Hüftgelenkspfanne, ausgewählt ist.

19. Implantierbare Lagerkomponente mit verbesserter Verschleißbeständigkeit, wobei die implantierbare Komponente ein bestrahltes vernetztes ultrahochmolekulares Polyethylen mit vermehrter Verschleißbeständigkeit und einer polymeren Struktur, **gekennzeichnet durch** 28% bis 51% Kristallinität, wie gemessen **durch** DSC, umfaßt.

20. Implantierbare Lagerkomponente nach Anspruch 19, wobei die Komponente weiterhin sterilisiert wird, wobei die Kristallinität wie nach der Sterilisation gemessen ist.

21. Implantierbare Lagerkomponente mit verbesserter Verschleißbeständigkeit, wobei die implantierbare Komponente ein vernetztes ultrahochmolekulares Polyethylen mit vermehrter Verschleißbeständigkeit umfaßt, wobei das ver- netzte ultrahochmolekulare Polyethylen eine polymere Struktur, **gekennzeichnet durch** weniger als 45% Kristal- linität, wie gemessen **durch** DSC, hat.

22. Implantierbare Lagerkomponente nach Anspruch 21, wobei das vernetzte ultrahochmolekulare Polyethylen eine polymere Struktur, **gekennzeichnet durch** zwischen 24% und 44% Kristallinität, wie gemessen **durch** DSC, hat.

23. Implantierbare Lagerkomponente nach Anspruch 21 oder 22, wobei die Komponente weiterhin sterilisiert wird.

24. Implantierbare Lagerkomponente nach Anspruch 23, wobei die Kristallinität wie nach der Sterilisation gemessen ist.

25. Implantierbare Lagerkomponente nach Anspruch 20 oder 24, wobei die Sterilisation mittels Bestrahlung erfolgt.

26. Implantierbare Lagerkomponente nach einem der Ansprüche 19 bis 25, wobei das vernetzte ultrahochmolekulare Polyethylen eine polymere Struktur, **gekennzeichnet durch** einen Quellungsgrad von 3,35, bereitgestellt **durch** Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% und nachfolgender Bestrahlung, oder eine polymere Struktur mit einem Quellungsgrad von 2,53 **durch** Vernetzen mit einer Peroxidkonzentration von 1 Gew.-%, hat.

27. Implantierbare Lagerkomponente nach einem der Ansprüche 19 bis 26, wobei das vernetzte ultrahochmolekulare

Polyethylen weiter **dadurch gekennzeichnet ist, daß** es (a) mit einer Peroxidkonzentration von 1 Gew.-% vernetzt worden ist und eine polymere Struktur von 99,6% oder fast 100% Gelgehalt aufweist oder (b) mit einer Peroxid-konzentration von 1 Gew.-% und nachfolgender Bestrahlung vernetzt worden ist und eine polymere Struktur von 97,5% Gelgehalt aufweist.

28. Implantierbare Lagerkomponente nach einem der Ansprüche 19 bis 27, wobei die Vernetzung nach dem Verfahren, ausgewählt aus der Gruppe, bestehend aus: chemischer Vernetzung eines Polyethylens, Strahlenvernetzung eines Polyethylens in einem geschmolzenen Zustand und Photovernetzung eines Polyethylens in einem geschmolzenen Zustand, erreicht wird.

29. Implantierbare Lagerkomponente nach einem der Ansprüche 19 bis 28, wobei die implantierbare Lagerkomponente in einer Gelenkprothese verwendet wird.

30. Implantierbare Lagerkomponente nach Anspruch 29, wobei die Gelenkprothese aus der Gruppe, bestehend aus: Hüft- und Kniegelenkprothesen, ausgewählt ist.

31. Implantierbare Lagerkomponente nach Anspruch 30, wobei die implantierbare Lagerkomponente aus der Gruppe, bestehend aus: einer Hüftgelenkspfanne, einem Einsatz einer Hüftgelenkspfanne und einer Einlage einer Hüftge-lenkspfanne, ausgewählt ist.

32. Verfahren zur Herstellung eines Implantats mit verbesserter Verschleißbeständigkeit, umfassend die Schritte: Ver-netzen eines Polyethylens, um ein bestrahltes vernetztes ultrahochmolekulares Polyethylen mit einer polymeren Struktur, **gekennzeichnet durch** 28% bis 5 1% Kristallinität, wie gemessen **durch** DSC, zu erzeugen und Tempern des vernetzten ultrahochmolekularen Polyethylens, um seine Größe vorzuschrumpfen und zu stabilisieren, bevor es zu einem Implantat verarbeitet wird.

33. Verfahren zur Herstellung eines Implantats mit verbesserter Verschleißbeständigkeit, umfassend die Schritte: Ver-netzen eines Polyethylens, um ein vernetztes ultrahochmolekulares Polyethylen mit einer polymeren Struktur, **gekennzeichnet durch** weniger als 45% Kristallinität, wie gemessen **durch** DSC, zu erzeugen, und Tempern des vernetzten ultrahochmolekularen Polyethylens, um seine Größe vorzuschrumpfen und zu stabilisieren, bevor es zu einem Implantat verarbeitet wird.

34. Verfahren nach Anspruch 33, wobei die polymere Struktur durch zwischen 24% und 44% Kristallinität, wie gemes-sen durch DSC, **gekennzeichnet** ist.

35. Verfahren nach einem der Ansprüche 32 bis 34 einschließlich eines Sterilisationsschrittes, wobei die Kristallinität wie nach dem Sterilisationsschritt gemessen ist.

36. Verfahren nach Anspruch 35, wobei der Sterilisationsschritt mittels Bestrahlung erreicht wird.

37. Verfahren nach einem der Ansprüche 32 bis 36, wobei die polymere Struktur durch eine Quellungsgrad von 3,35, bereitgestellt durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% und Bestrahlung, oder einen Quel-lungsgrad von 2,53 durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% **gekennzeichnet** ist.

38. Verfahren nach einem der Ansprüche 32 bis 37, wobei das vernetzte ultrahochmolekulare Polyethylen weiter **da-durch gekennzeichnet ist, daß** es (a) mit einer Peroxidkonzentration von 1 Gew.-% vernetzt worden ist und eine polymere Struktur von 99,6% oder fast 100% Gelgehalt aufweist oder (b) mit einer Peroxidkonzentration von 1 Gew.-% und nachfolgender Bestrahlung vernetzt worden ist und eine polymere Struktur von 97,5% Gelgehalt aufweist.

39. Verfahren nach einem der Ansprüche 32 bis 38, wobei das Implantat eine Komponente zur Verwendung in einer Gelenkprothese ist.

40. Verfahren nach einem der Ansprüche 32 bis 39, wobei das Implantat eine Lagerkomponente ist.

41. Verfahren nach einem der Ansprüche 32 bis 40, wobei das Implantat aus der Gruppe, bestehend aus: einer Hüft-gelenkspfanne, einem Einsatz einer Hüftgelenkspfanne und einer Einlage einer Hüftgelenkspfanne, ausgewählt ist.

42. Verfahren zur Verbesserung der Verschleißbeständigkeit eines Implantats zur Verwendung innerhalb eines Körpers, wobei das Implantat aus bestrahltem vernetzten ultrahochmolekularen Polyethylen hergestellt ist, wobei das Verfahren den Schritt der Vernetzung eines Polyethylens umfaßt, um eine polymere Struktur zwischen 28% und 51% Kristallinität wie gemessen durch DSC, bereitzustellen.

43. Verfahren zur Verbesserung der Verschleißbeständigkeit eines Implantats zur Verwendung innerhalb eines Körpers, wobei das Implantat aus bestrahltem vernetzten ultrahochmolekularen Polyethylen hergestellt ist, wobei das Verfahren den Schritt der Vernetzung eines Polyethylens umfaßt, um eine polymere Struktur mit weniger als 45% Kristallinität, wie gemessen durch DSC, bereitzustellen.

44. Verfahren nach Anspruch 43, wobei die polymere Struktur durch zwischen 24% und 44% Kristallinität, wie gemessen durch DSC, **gekennzeichnet** ist.

45. Verfahren nach einem der Ansprüche 42 bis 44, weiterhin umfassend den Schritt der Sterilisierung des Implantats, wobei die Kristallinität wie nach der Sterilisation gemessen ist.

46. Verfahren nach Anspruch 45, wobei die Sterilisation mittels Bestrahlung erfolgt.

47. Verfahren nach einem der Ansprüche 42 bis 46, wobei die polymere Struktur durch einen Quellungsgrad von 3,35, bereitgestellt durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% und Bestrahlung, oder einen Quellungsgrad von 2,53 durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% **gekennzeichnet** ist.

48. Verfahren nach einem der Ansprüche 42 bis 47, wobei das vernetzte ultrahochmolekulare Polyethylen weiter **dadurch gekennzeichnet ist, daß** es (a) mit einer Peroxidkonzentration von 1 Gew.-% vernetzt worden ist und eine polymere Struktur von 99,6% oder fast 100% Gelgehalt aufweist oder (b) mit einer Peroxidkonzentration von 1 Gew.-% und nachfolgender Bestrahlung vernetzt worden ist und eine polymere Struktur von 97,5% Gelgehalt aufweist.

49. Verfahren nach einem der Ansprüche 42 bis 48, wobei das Implantat eine Komponente zur Verwendung in einer Gelenkprothese ist.

50. Verfahren nach einem der Ansprüche 42 bis 49, wobei das Implantat eine prothetische Lagerkomponente ist.

51. Verfahren nach einem der Ansprüche 42 bis 50, wobei das Implantat aus der Gruppe, bestehend aus: einer Hüftgelenkspfanne, einem Einsatz einer Hüftgelenkspfanne und einer Einlage einer Hüftgelenkspfanne, ausgewählt ist.

52. Verfahren zur Herstellung und Verbesserung der Verschleißfestigkeit eines Implantats zur Verwendung innerhalb eines Körpers, umfassend die Schritte: (a) Vernetzen eines Polyethylens, um ein bestrahltes vernetztes ultrahochmolekulares Polyethylen mit einer polymeren Struktur von zwischen 28% und 51% Kristallinität, wie gemessen durch DSC, bereitzustellen, und (b) Erzeugen des Implantats aus dem vernetzten ultrahochmolekularen Polyethylen.

53. Verfahren zur Herstellung und Verbesserung der Verschleißfestigkeit eines Implantats zur Verwendung innerhalb eines Körpers, umfassend die Schritte: (a) Vernetzen eines Polyethylens, um ein vernetztes ultrahochmolekulares Polyethylen mit einer polymeren Struktur von weniger als 45% Kristallinität, wie gemessen durch DSC, bereitzustellen, und (b) Erzeugen des Implantats aus dem vernetzten ultrahochmolekularen Polyethylen.

54. Verfahren nach Anspruch 53, wobei die polymere Struktur durch zwischen 24% und 44% Kristallinität, wie gemessen durch DSC, **gekennzeichnet** ist.

55. Verfahren nach einem der Ansprüche 52 bis 54, wobei der Schritt der Vernetzung weiterhin das vernetzte ultrahochmolekulare Polyethylen mit einer polymeren Struktur mit einem Quellungsgrad von 3,35, bereitgestellt durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% und Bestrahlung, oder einem Quellungsgrad von 2,53, bereitgestellt durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-%, bereitstellt.

56. Verfahren nach einem der Ansprüche 52 bis 55, wobei der Schritt der Vernetzung (a) durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% erfolgt und weiterhin das ultrahochmolekulare Polyethylen mit einer polymeren

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Struktur von 99,6% oder fast 100% Gelgehalt bereitstellt oder (b) durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% und nachfolgender Bestrahlung erfolgt und weiterhin das ultrahochmolekulare Polyethylen mit einer polymeren Struktur von 97,5% Gelgehalt bereitstellt.

57. Verfahren nach einem der Ansprüche 52 bis 56, wobei das Implantat eine Komponente zur Verwendung in einer Gelenkprothese ist.

58. Verfahren nach einem der Ansprüche 52 bis 57, wobei das Implantat eine prothetische Lagerkomponente ist.

59. Verfahren nach einem der Ansprüche 52 bis 58, wobei das Implantat aus der Gruppe, bestehend aus: einer Hüftgelenkspfanne, einem Einsatz einer Hüftgelenkspfanne und einer Einlage einer Hüftgelenkspfanne, ausgewählt ist.

60. Verfahren nach einem der Ansprüche 52 bis 59, weiterhin umfassend den Schritt des Temperns des vernetzten ultrahochmolekularen Polyethylens bei einer Temperatur von 60°C bis 120°C für 1 bis 6 Stunden, um seine Größe zu stabilisieren.

Revendications

1. Implant à utiliser dans un corps, ledit implant étant fait de polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ayant une structure polymère d'une cristallinité d'entre 28% et 51%, telle que mesurée par DSC, de manière à augmenter la résistance à l'usure dudit implant dans le corps.

2. L'implant de la revendication 1, où l'implant est en outre stérilisé, la cristallinité étant mesurée après la stérilisation.

3. Implant à utiliser dans un corps, ledit implant étant fait d'un polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ayant une structure polymère d'une cristallinité de moins de 45%, telle que mesurée par DSC, de manière à augmenter la résistance à l'usure dudit implant dans le corps.

4. L'implant de la revendication 3, où ledit polyéthylène de poids moléculaire ultra élevé a une cristallinité d'entre 24% et 44%, telle que mesurée par DSC.

5. L'implant de la revendication 3 ou 4, où l'implant est en outre stérilisé.

6. L'implant de la revendication 5, où la cristallinité est telle que mesurée après la stérilisation.

7. L'implant de la revendication 2 ou 5, où ladite stérilisation est faite par irradiation.

8. L'implant de l'une quelconque des revendications précédentes, où ledit polyéthylène de poids moléculaire ultra élevé, réticulé, est **caractérisé en** outre (a) en ayant été réticulé avec une concentration de peroxyde de 1% en poids et en ayant une structure polymère d'une teneur en gel de 99,6% ou de presque 100%, ou (b) en ayant été réticulé avec une concentration de peroxyde de 1% en poids, suivi par l'irradiation et en ayant une structure polymère d'une teneur en gel de 97,5%.

9. L'implant de l'une quelconque des revendications précédentes, où la réticulation est réalisée selon le procédé sélectionné parmi le groupe consistant à: réticuler chimiquement un polyéthylène, réticuler par irradiation un polyéthylène dans un état fondu, et photoréticuler un polyéthylène dans un état fondu.

10. L'implant de la revendication 7, où ledit implant est irradié à l'état solide.

11. L'implant de la revendication 10, où ledit implant est irradié à l'air avec un rayonnement gamma à une dose de 34 kGy.

12. L'implant de l'une quelconque des revendications précédentes, où ledit polyéthylène de poids moléculaire ultra élevé, réticulé, est en outre **caractérisé en** ayant été recuit de manière à le rétrécir à une dimension stable.

13. L'implant de l'une quelconque des revendications précédentes, où ledit polyéthylène de poids moléculaire ultra

élevé, réticulé, est en outre **caractérisé par** une structure polymère d'un degré de gonflement de 3,35 fourni par la réticulation avec une concentration de peroxyde de 1% en poids, suivie par l'irradiation, ou par une structure polymère d'un degré de gonflement de 2,53 par la réticulation avec une concentration de peroxyde de 1% en poids.

14. L'implant de l'une quelconque des revendications précédentes, où l'implant est un composant à utiliser dans une prothèse articulaire.

15. L'implant de la revendication 14, où le composant est un composant porteur.

16. L'implant de la revendication 14 ou 15, où la prothèse articulaire est sélectionnée du groupe consistant en: prothèses articulaires de la hanche, du genou, de la cheville, du coude, de la mâchoire, de l'épaule, du doigt et en prothèses articulaires facettaires rachidiennes.

17. L'implant de la revendication 16, où la prothèse articulaire est sélectionnée parmi le groupe consistant en: prothèses articulaires de la hanche et du genou.

18. L'implant de la revendication 17, où l'implant est sélectionné parmi le groupe consistant en: une cupule cotyloïdienne, un insert de cupule cotyloïdienne et une garniture de cupule cotyloïdienne.

19. Composant porteur implantable avec une résistance à l'usure améliorée, ledit composant implantable comprenant un polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ayant une résistance à l'usure augmentée, et une structure polymère **caractérisée par** une cristallinité de 28% à 51%, telle que mesurée par DSC.

20. Le composant porteur implantable de la revendication 19, où le composant est en outre stérilisé, la cristallinité étant telle que mesurée après la stérilisation.

21. Composant porteur implantable avec une résistance à l'usure améliorée, ledit composant implantable comprenant un polyéthylène de poids moléculaire ultra élevé, réticulé, ayant une résistance à l'usure augmentée, ledit polyéthylène de poids moléculaire ultra élevé, réticulé, ayant une structure polymère **caractérisée par** une cristallinité de moins de 45%, telle que mesurée par DSC.

22. Le composant porteur implantable de la revendication 21, où le polyéthylène de poids moléculaire ultra élevé, réticulé, a une structure polymère **caractérisée par** une cristallinité d'entre 24% et 44%, telle que mesurée par DSC.

23. Le composant porteur implantable de la revendication 21 ou 22, où le composant est en outre stérilisé.

24. Le composant porteur implantable de la revendication 23, où ladite cristallinité est telle que mesurée après la stérilisation.

25. Le composant porteur implantable de la revendication 20 ou 24, où ladite stérilisation est faite par irradiation.

26. Le composant porteur implantable de l'une quelconque des revendications 19 à 25, où le polyéthylène de poids moléculaire ultra élevé, réticulé, a une structure polymère **caractérisée par** un degré de gonflement de 3,35 fourni par la réticulation avec une concentration de peroxyde de 1% en poids, suivie par l'irradiation, ou une structure polymère d'un degré de gonflement de 2,53 par la réticulation avec une concentration de peroxyde de 1% en poids.

27. Le composant porteur implantable de l'une quelconque des revendications 19 à 26, où le polyéthylène de poids moléculaire ultra élevé, réticulé, est **caractérisé en** outre (a) en ayant été réticulé avec une concentration de peroxyde de 1% en poids et en ayant une structure polymère d'une teneur en gel de 99,6% ou de presque 100%, ou (b) en ayant été réticulé avec une concentration de peroxyde de 1% en poids, suivi par l'irradiation et en ayant une structure polymère d'une teneur en gel de 97,5%.

28. Le composant porteur implantable de l'une quelconque des revendications 19 à 27, où la réticulation est réalisée selon le procédé sélectionné parmi le groupe consistant à: réticuler chimiquement un polyéthylène, réticuler par irradiation un polyéthylène dans un état fondu, et photoréticuler un polyéthylène dans un état fondu.

29. Le composant porteur implantable de l'une quelconque des revendications 19 à 28, où le composant porteur implantable est utilisé dans une prothèse articulaire.

30. Le composant porteur implantable de la revendication 29, où la prothèse articulaire est sélectionnée parmi le groupe consistant en: prothèses articulaires de la hanche et du genou.

31. Le composant porteur implantable de la revendication 30, où le composant porteur implantable est sélectionné parmi le groupe consistant en: une cupule cotyloïdienne, un insert de cupule cotyloïdienne et une garniture de cupule cotyloïdienne.

32. Procédé de production d'un implant avec une résistance à l'usure améliorée, comprenant les étapes consistant à: réticuler un polyéthylène pour produire un polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ayant une structure polymère **caractérisée par** une cristallinité de 28% à 51%, telle que mesurée par DSC, et recuire le polyéthylène de poids moléculaire ultra élevé, réticulé, pour prérétrécir et stabiliser sa dimension avant de le transformer en un implant.

33. Procédé de production d'un implant avec une résistance à l'usure améliorée, comprenant les étapes consistant à: réticuler un polyéthylène pour produire un polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ayant une structure polymère **caractérisée par** une cristallinité de moins de 45%, telle que mesurée par DSC, et recuire le polyéthylène de poids moléculaire ultra élevé, réticulé, pour prérétrécir et stabiliser sa dimension avant de le transformer en un implant.

34. Le procédé de la revendication 33, où la structure polymère est **caractérisée par** une cristallinité d'entre 24% et 44%, telle que mesurée par DSC.

35. Le procédé de l'une quelconque des revendications 32 à 34 comprenant une étape de stérilisation, où la cristallinité est telle que mesurée après l'étape de stérilisation.

36. Le procédé tel que revendiqué dans la revendication 35, où l'étape de stérilisation est réalisée par irradiation.

37. Le procédé de l'une quelconque des revendications 32 à 36, où la structure polymère est **caractérisée par** un degré de gonflement de 3,35 fourni par la réticulation avec une concentration de peroxyde de 1% en poids et l'irradiation, ou un degré de gonflement de 2,53 par la réticulation avec une concentration de peroxyde de 1% en poids.

38. Le procédé de l'une quelconque des revendications 32 à 37, où ledit polyéthylène de poids moléculaire ultra élevé, réticulé, est **caractérisé en** outre (a) en ayant été réticulé avec une concentration de peroxyde de 1% en poids et en ayant une structure polymère d'une teneur en gel de 99,6% ou de presque 100%, ou (b) en ayant été réticulé avec une concentration de peroxyde de 1% en poids, suivi par l'irradiation et en ayant une structure polymère d'une teneur en gel de 97,5%.

39. Le procédé de l'une quelconque des revendications 32 à 38, où l'implant est un composant à utiliser dans une prothèse articulaire.

40. Le procédé de l'une quelconque des revendications 32 à 39, où l'implant est un composant porteur.

41. Le procédé de l'une quelconque des revendications 32 à 40, où l'implant est sélectionné parmi le groupe consistant en: une cupule cotyloïdienne, un insert de cupule cotyloïdienne et une garniture de cupule cotyloïdienne.

42. Procédé pour améliorer la résistance à l'usure d'un implant à utiliser dans un corps, ledit implant étant fait de polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ledit procédé comprenant l'étape consistant à réticuler un polyéthylène pour donner une structure polymère d'une cristallinité d'entre 28% et 51 %, telle que mesurée par DSC.

43. Procédé pour améliorer la résistance à l'usure d'un implant à utiliser dans un corps, ledit implant étant fait de polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ledit procédé comprenant l'étape consistant à réticuler un polyéthylène pour donner une structure polymère avec une cristallinité de moins de 45%, telle que mesurée par DSC.

44. Le procédé de la revendication 43, où la structure polymère est **caractérisée par** une cristallinité d'entre 24% et 44%, telle que mesurée par DSC.

45. Le procédé de l'une quelconque des revendications 42 à 44, comprenant en outre l'étape consistant à stériliser l'implant, où la cristallinité est telle que mesurée après la stérilisation.

46. Le procédé de la revendication 45, où la stérilisation est faite par irradiation

47. Le procédé de l'une quelconque des revendications 42 à 46, où la structure polymère est **caractérisée par** un degré de gonflement de 3,35 fourni par la réticulation avec une concentration de peroxyde de 1% en poids et l'irradiation, ou un degré de gonflement de 2,53 par la réticulation avec une concentration de peroxyde de 1% en poids.

48. Le procédé de l'une quelconque des revendications 42 à 47, où ledit polyéthylène de poids moléculaire ultra élevé, réticulé, est **caractérisé en** outre (a) en ayant été réticulé avec une concentration de peroxyde de 1% en poids et en ayant une structure polymère d'une teneur en gel de 99,6% ou de presque 100%, ou (b) en ayant été réticulé avec une concentration de peroxyde de 1% en poids, suivi par l'irradiation et en ayant une structure polymère d'une teneur en gel de 97,5%.

49. Le procédé de l'une quelconque des revendications 42 à 48, où l'implant est un composant à utiliser dans une prothèse articulaire.

50. Le procédé de l'une quelconque des revendications 42 à 49, où l'implant est un composant prothétique porteur.

51. Le procédé de l'une quelconque des revendications 42 à 50, où l'implant est sélectionné parmi le groupe consistant en: une cupule cotyloïdienne, un insert de cupule cotyloïdienne et une garniture de cupule cotyloïdienne.

52. Procédé pour faire et améliorer la résistance à l'usure d'un implant à utiliser dans un corps, comprenant les étapes consistant à: (a) réticuler un polyéthylène pour fournir un polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, avec une structure polymère d'une cristallinité d'entre 28% et 51%, telle que mesurée par DSC, et (b) former l'implant avec ledit polyéthylène de poids moléculaire ultra élevé, réticulé.

53. Procédé pour faire et améliorer la résistance à l'usure d'un implant à utiliser dans un corps, comprenant les étapes consistant à: (a) réticuler un polyéthylène en un polyéthylène de poids moléculaire ultra élevé, réticulé, irradié avec une structure polymère d'une cristallinité de moins de 45%, telle que mesurée par DSC, et (b) former l'implant avec ledit polyéthylène de poids moléculaire ultra élevé, réticulé.

54. Le procédé de la revendication 53, où la structure polymère est **caractérisée par** une cristallinité d'entre 24% et 44%, telle que mesurée par DSC.

55. Le procédé de l'une quelconque des revendications 52 à 54, où l'étape de réticulation fournit en outre au polyéthylène de poids moléculaire ultra élevé, réticulé, une structure polymère d'un degré de gonflement de 3,35 fourni par la réticulation avec une concentration de peroxyde de 1% en poids et l'irradiation, ou un degré de gonflement de 2,53 fourni par la réticulation avec une concentration de peroxyde de 1% en poids.

56. Le procédé de l'une quelconque des revendications 52 à 55, où l'étape de réticulation se fait (a) par la réticulation avec une concentration de peroxyde de 1% en poids et fournit en outre au polyéthylène de poids moléculaire ultra élevé, une structure polymère d'une teneur en gel de 99,6% ou de presque 100%, ou (b) par la réticulation avec une concentration de peroxyde de 1% en poids suivie par l'irradiation, et fournit en outre au polyéthylène de poids moléculaire ultra élevé, une structure polymère d'une teneur en gel de 97,5%.

57. Le procédé de l'une quelconque des revendications 52 à 56, où l'implant est un composant à utiliser dans une prothèse articulaire.

58. Le procédé de l'une quelconque des revendications 52 à 57, où l'implant est un composant prothétique porteur.

59. Le procédé de l'une quelconque des revendications 52 à 58, où l'implant est sélectionné parmi le groupe consistant en: une cupule cotyloïdienne, un insert de cupule cotyloïdienne et une garniture de cupule cotyloïdienne.

60. Le procédé de l'une quelconque des revendications 52 à 59, comprenant en outre l'étape consistant à recuire le polyéthylène de poids moléculaire ultra élevé, réticulé, à une température de 60°C à 120°C pendant 1 à 6 heures pour en stabiliser la dimension.

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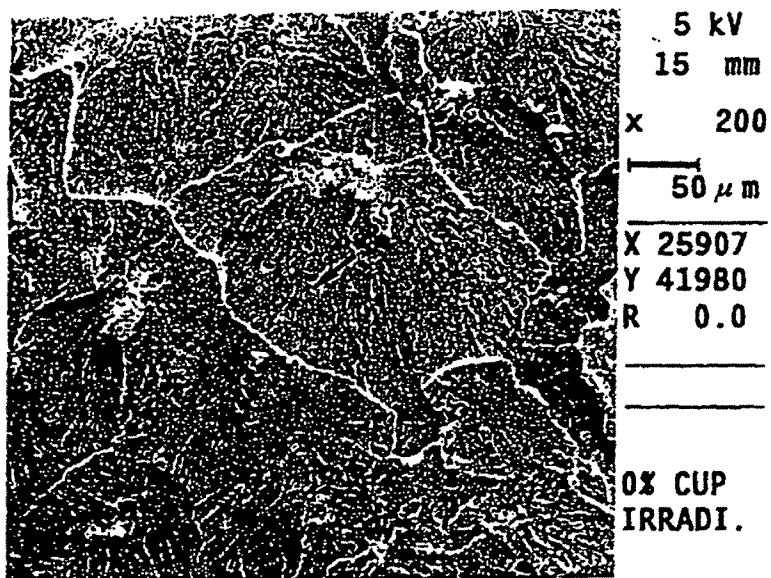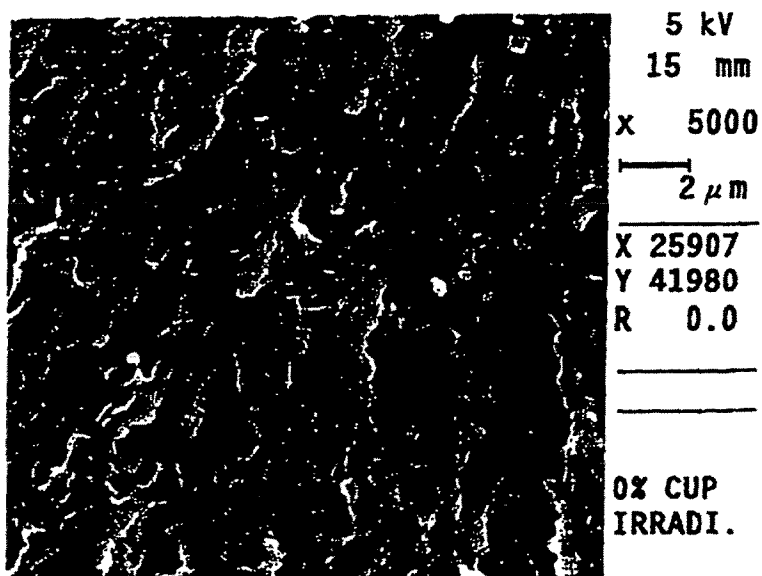*20*

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FIG. 1A


```
  5 kV
 15   mm
x    200
    50 μm
X 25907
Y 41980
R    0.0


0% CUP
IRRADI.
```

FIG. 1B


```
  5 kV
 15   mm
x   5000
     2 μm
X 25907
Y 41980
R    0.0


0% CUP
IRRADI.
```

FIG. 2A

5 kV
.14 mm
x 200
⊢——⊣ 50 μm
X 32178
Y 24709
R 0.0

1% CUP
IRRADI.

FIG. 2B

5 kV
14 mm
x 5000
⊢——⊣ 2 μm
X 32178
Y 24709
R 0.0

1% CUP
IRRADI.

FIG. 3A

3B

3B

FIG. 3B

4

1

2

3
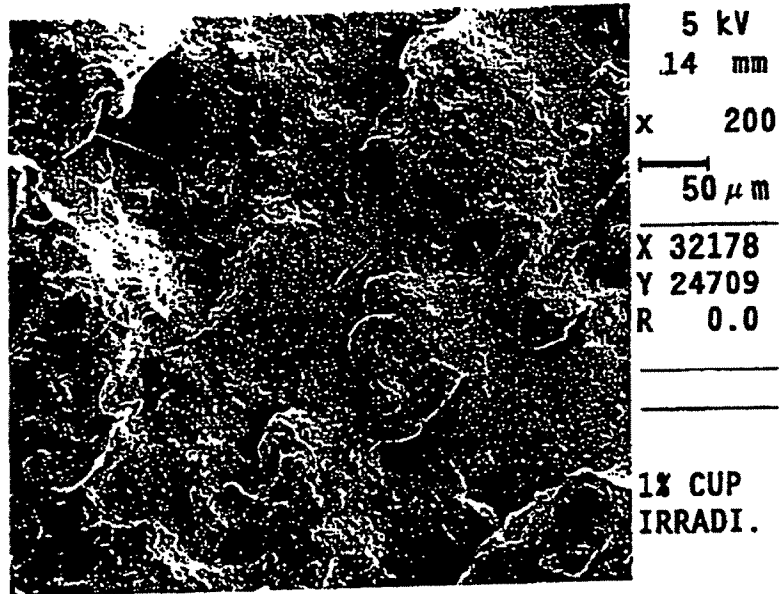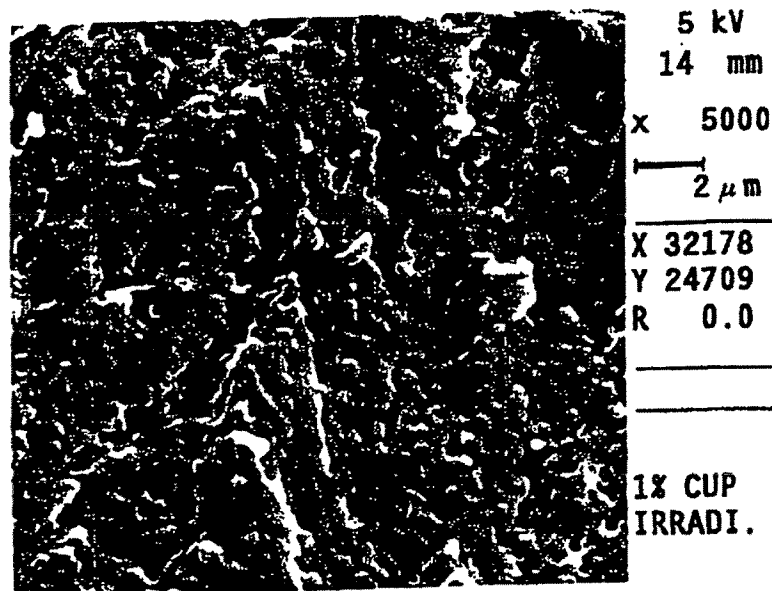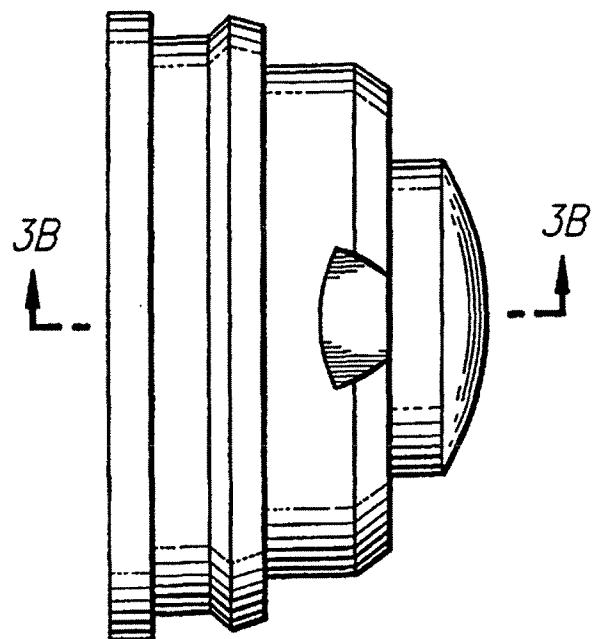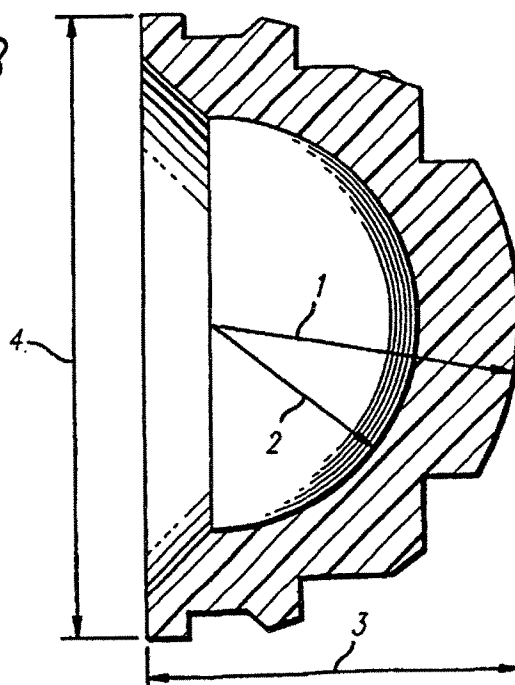
FIG. 4

FIG. 5

(12) EUROPEAN PATENT SPECIFICATION

(54) **ULTRAHIGH-MOLECULAR-WEIGHT POLYETHYLENE MOLDING FOR ARTIFICIAL JOINT AND PROCESS FOR PRODUCING THE MOLDING**

POLYETHYLENGUSS MIT ULTRAHOHEM MOLEKULARGEWICHT FÜR KÜNSTLICHE VERBINDUNGEN UND VERFAHREN ZU DESSEN HERSTELLUNG

PIECE MOULEE EN POLYETHYLENE A POIDS MOLECULAIRE ULTRA ELEVE UTILE POUR LES ARTICULATIONS ARTIFICIELLES ET SON PROCEDE DE FABRICATION

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(56) References cited:
JP-A- 4 198 201   JP-A- 62 243 634
US-A- 4 587 163   US-A- 4 747 990
US-A- 5 030 402

• **EDIT BY POLYMER SOCIETY, "Polymer Functional Material Series (Vol. 9), Medical Treatment Functional Material", 20 November 1990, KYORITSU SHUPPAN K.K., p.165-166.**
• **EDIT BY POLYMER SOCIETY, "Polymer New Material One Point (Vol. 20), Medical Polymer Material", 20 February 1989, KYORITSU SHUPPAN K.K., p. 45-46.**

EP 0 729 981 B1

Description

TECHNICAL FIELD

[0001]   The present invention relates to an ultra high molecular weight polyethylene molded article suitable for artificial joints having crystal orientation and to a method of preparing the same.

BACKGROUND ART

[0002]   It has been passed thirty years or more since an artificial joint was developed and applied clinically to patients suffering from any diseases of arthritis. Since then, benefits given by the artificial joint have been great in the sense of social welfare because, for example, patients with chronic rheumatism have come to be able to walk again and to return to public life. On the other hand, however, there have occurred serious problems, particularly late complications caused by total joint arthroplasty, a high rate of occurrance of "loosening" in the implant components, necessity of revision with surgical operation caused by osteolysis around the implanted artificial joint.

[0003]   The artificial joint includes artificial hip joint, artificial knee joint, artificial elbow joint, artificial finger joint, artificial shoulder joint and the like. Among those joints, it is necessary for the artificial hip joint and artificial knee joint to have high mechanical strength because gravity corresponding to several times of the patient's body weight is applied to them. Therefore, materials for the artificial joint at present are constituted of a hard material of metal or ceramic and a soft socket of an ultra high molecular weight polyethylene (UHMWPE). While the UHMWPE constituting such a socket is superior in abrasion resistance as compared with polymeric materials such as polytetrafluoroethylene and polycarbonate, the UHMWPE is inferior in properties such as low abrasion resistance and stress relaxation to impact load which are inherently possessed by articular cartilage of living body. Also, reaction caused by a foreign matter has been a serious problem wherein macrophages proliferate against wear debris of the UHMWPE socket, i.e. component and an abnormal granulation tissue generated thereby causes resorption of the bone.

[0004]   After artificial joints have been developed, though some improvements in qualities of material and design have been made, for example, a cementless artificial joint and the like with respect to the hard material, there has been no remarkable progress for about thirty years with respect to the soft socket portion except that the UHMWPE was employed. And if the artificial joint is used for a long period of time, numerous wear debris of polyethylene are produced because of friction between the hard material such as metal and the UHMWPE of the socket. By considering the osteolysis due to granulation tissue containing a foreign matter which is caused by the wear debris, further improvement of abrasion resistance is indispensable. As an attempt to reduce the abrasion of UHMWPE, it can be considered to select a material for the hard material and to improve the UHMWPE. Though the irradiation of an ultra high dose of γ-ray was tried for improving the UHMWPE, it was made clear that the coefficient of abrasion increases and abrasion loss does not decrease. Also, though the improvement to increase molecular weight of the UHMWPE was made and the weight-average molecular weight of the UHMWPE at present has been increased to approximately 5 to 8 million, it is difficult to make a UHMWPE having a far ultra high molecular weight. Further, considerable improvement in dynamic properties can scarcely be expected even if one having a weight-average molecular weight of 10 million could be synthesized. Thus, it is regarded that any improvement in dynamic properties of the UHMWPE by chemical modification reaches its limitation, and it is regarded to be difficult to obtain a UHMWPE molded article having a more excellent abrasion resistance and lower friction.

[0005]   It is well-known that Carothers of E.I. Du Pont developed, first all over the world, a synthetic fiber, i.e. Nylon and greatly contributed industrially. As means for improving mechanical properties of this synthetic fiber, uniaxial stretching in the direction of fiber axis is carried out industrially. Also, to improve strength of film, biaxial stretching and rolling are carried out industrially. In accordance with these methods, mechanical properties can be increased considerably by giving uniaxial orientation or biaxial orientation to molecules or crystals.

[0006]   From these points of view, there is an idea that orientation is given to molecules or crystals in the polymer structure to improve the mechanical properties. However, any technologies cannot endow molecules or crystals with orientation in a large molded article in the form of block, and it is not easy to consider an enable method.

[0007]   Then, the present inventors tried to obtain a molded article of a low friction and to improve an abrasion resistance by introducing crystal orientation into a finished product by means of not a chemical modification method but a physical modification method.

[0008]   This approach has never been attempted not only in Japan but also in other countries. The idea to endow the polyethylene molded article for artificial joints with molecular orientation or crystal orientation is the very creative, and it is sure that this invention, if actually carried out, is applied to the artificial joints of all over the world. Also, this invention will be a revolutionary industrial innovation whereby disadvantages which have been a problem for the past thirty years are improved

DISCLOSURE OF THE INVENTION

[0009] The invention relates to an ultra high molecular weight polyethylene (UHMWPE) molded article for artificial joints and to an artificial joint comprising the UHMWPE molded article.

5 [0010] This UHMWPE molded article having crystal orientation can be obtained by irradiating a low dose of a high energy ray to a raw UHMWPE molded article to introduce a very small amount of crosslinking points in polymer chains to be crosslinked slightly, then by compression-deforming the crosslinked UHMWPE molded article after heating up to its compression-deformable temperature, and by cooling the molded article with keeping the deformed state.

[0011] The UHMWPE molded article having crystal orientation (hereinafter referred to as "oriented UHMWPE molded 10 article") of the present invention has a low friction and remarkably improved abrasion resistance. And, the artificial joint comprising the oriented UHMWPE molded article has a smooth lubricity and reduced amount of abrasion loss.

BEST MODE FOR CARRYING OUT INVENTION

15 [0012] The oriented UHMWPE molded article of the invention has the crystal orientation within the molded article. The meaning of "to have crystal orientation" is that the crystal planes in polyethylene such as (200) plane and (110) plane are oriented to the direction parallel to the compression plane, namely, that the crystal planes are oriented. Also, the presence of these orientations can be known by means of birefringence measurements, infrared spectra and X-ray diffraction. And, a coefficient of friction of the molded article decreases and an abrasion loss also decreases by 20 endowing with those orientations. Also, other functional properties, for example, tensile strength and tensile modulus are improved, and also density, thermal properties (melting point, heat of fusion) and the like are improved.

[0013] As described above, the oriented UHMWPE molded article can be obtained by irradiating a high energy ray to the raw UHMWPE and then heating up and compression-deforming the UHMWPE, followed by cooling and solidifying.

25 [0014] As the raw UHMWPE, one having a weight-average molecular weight of 2 to 8 million, preferably 5 to 7 million is used. The melting point thereof is approximately 136° to 139°C. The raw UHMWPE is used in the form of a block.

[0015] Every kind of high energy rays can be employed as the high energy ray to be irradiated, for example a radioactive ray such as γ-ray or X-ray, an electron beam, a neutron ray and the like. Among them, γ-ray is superior in view of availability of irradiation apparatus and excellent permeability to materials. This irradiation of the high energy ray is 30 carried out to generate crosslinking points in the molecular chains of the UHMWPE and then to produce intermolecular crosslinkage. The density of crosslinking is preferably such a very small degree that the crystallization is not prevented with ensuring a large elastic-deformation, for example 0.1 to 10, particularly 1 to 2 crosslinking points per one molecular chain.

[0016] With respect to the irradiation atmosphere, if oxygen exists, it is not preferable since a decomposition (cleav-35 age) occurs simultaneously, and therefore the atmosphere in vacuum or of an inert gas such as N_2 or argon is preferable. The temperature of the atmosphere may be room temperature and also may be a higher temperature of not less than the crystal transition point (80°C).

[0017] The dose of irradiation (energy) is very important. If the dose of irradiation is too high, the density of crosslinking becomes higher, and the bridged structure is destroyed if a large deformation is applied in the subsequent process. 40 And, even if the molten state is made, such a degree of elastic deformation required to obtain the desired crystal orientation cannot be givenL As a result, it is obliged to decrease a degree of the deformation, and it becomes impossible to obtain the crystal orientation which is necessary for molecular chains in the molded article. On the other hand, in case that a dose of irradiation is too low or no irradiation is carried out, molecular chains are fluidized in the manner of viscous fluidity without stretching to be plastic-deformed, resulting in that the molecular orientation or crystal orien-45 tation cannot be obtained. A preferable dose of irradiation (energy) is the dose to give the above-mentioned density of crosslinking and 100 to 50,000 J/kg (0.01 to 5.0 MR), preferably 1000 to 30,000 J/kg (0.1 to 3 MR) in case of radioactive rays.

[0018] The UHMWPE molded article which is crosslinked slightly by irradiating the high energy ray has an infinite weight-average molecular weight because it is crosslinked, and the melting point thereof changes not so much and is 50 136° to 139°C.

[0019] Then, this slightly crosslinked UHMWPE molded article is heated up to a compression-deformable temperature. The compression-deformable temperature is a temperature of around or not less than the melting point of the crosslinked UHMWPE, and is concretely from the melting point minus 50°C to the melting point plus 80°C. It is most suitable to heat up to a temperature of not less than the melting point, particularly preferably 160° to 220°C, further 55 preferably 180° to 200°C to melt completely. The compression-deformation can be carried out, however, at a temperature of even around the melting point, for example 100° to 130°C. If completely melted, since the crosslinked UHMWPE is in the state of rubber to possess rubber elasticity, the compression-deformation is easily carried out.

[0020] The compression-deformation is carried out under a pressure of 3.10^5 to 2.10^6 Pa (30 to 200 kgf/cm^2), usually

5.10^5 to 10^6 Pa (50 to 100 kgf/cm^2) with heating at the above-mentioned temperature in a die suitable for the use or by using a hot press machine. It is sufficient that a degree of the compression is approximately 1/3 to 1/10 of an original thickness in case of a molded article in the form of block The deformation of the crosslinked UHMWPE molded article of the present invention is a rubber elastic deformation because molecular chains are crosslinked slightly, and after the molecular chains are stretched to give the necessary molecular orientation, then cooled as they are and crystallized, the crystal orientation can be obtained. On the other hand, non-crosslinked, namely non-irradiated UHMWPE molded article is fluid-deformed when heated and compressed at a temperature of not less than the melting point, and thus crystal orientation cannot be obtained.

[0021] Then, the UHMWPE molded article having the crystal orientation obtained by the compression-deformation as described above is cooled and solidified with keeping the deformed state. If the deformed state is set free before solidified, the stretched molecular chains are relaxed in stress to return to the original state because the compression-deformation is conducted in the molten state. That is, the molecular orientation or crystal orientation in the UHMWPE molded article is relaxed in a moment. Therefore, the deformed state must not be set free until solidified.

[0022] As the cooling method, there are rapid coolings such as water-cooling and air-cooling as well as standing to cool, and the cooling is carried out down to room temperature, preferably to a temperature of around 20° to 40°C. Further, it is preferable to cool at a constant rate under a condition of 10°C/min, preferably 1°C/min to obtain excellent dynamic properties because the cooling rate has a great influence on the crystallinity, particularly on the degree of crystallinity of the produced molded article. The completion of the solidification can be confirmed by decrease of a pressure gauge (the volume being shrinked after the completion of the crystallization).

[0023] Also, before the cooling the compression-deformed UHMWPE molded article may be subjected to isothermal crystallization at around 100° to 130°C, preferably 110° to 120°C for 1 to 20 hours, preferably 5 to 10 hours with keeping the deformed state, and then cooled to room temperature, preferably to 40°C and solidified. When carrying out the isothermal crystallization, the degree of crystallinity becomes higher and the dynamic properties are improved. The cooling after the isothermal crystallization is not particularly limited and the cooling at a rate of 1°C/min is preferable.

[0024] The melting point of the UHMWPE molded article having the crystal orientation obtained by the cooling and solidification is 135° to 155°C.

[0025] The compression-deformed molded article which is obtained as described above can also be processed to a socket for artificial joints by cutting and can be molded by means of the compression-deformation mold with a die comprising a convex and concave portions. The surface hardness can be further reinforced by introducing metal ions, e.g. titanium, zirconium, iron, molybdenum, aluminium and/or cobalt ion into the UHMWPE molded article for artificial joints which is obtained by cutting the compression-deformed molded article.

[0026] Hereinafter, the present invention is explained concretely by referring to Preparation Examples and Examples.

PREPARATION EXAMPLES 1 TO 3

[0027] A block of UHMWPE (thickness 3 cm, width 5 cm, length 5 cm) having a weight-average molecular weight of approximately 6 million and a melting point: 138°C was put in a glass ampul and the glass was sealed after reducing the inner pressure (10^{-2} to 10^{-3} mmHg) under vacuum. γ-Ray from cobalt 60 was irradiated at a dose of 5,000 J/kg (0.5 MR) to this glass ampul at 25°C. Then, the UHMWPE block irradiated by the radioactive ray (melting point: 138°C, weight-average molecular weight: infinite) was taken out from the glass ampul, melted completely at 200°C by using a hot press, compressed to 1/3, 1/4.5 and 1/6 of the original thickness by applying a pressure of 50 kgf/cm^2, and then cooled to room temperature through natural cooling with keeping the deformed state.

COMPARATIVE PREPARATION EXAMPLES 1 TO 3

[0028] The same raw UHMWPE block as was used in Preparation Examples 1 to 3 was compressed to 1/3, 1/4.5 and 1/6 of the original thickness after melting completely at 200°C by using a hot press in the same way without irradiation, and cooled naturally to room temperature with keeping the deformed state.

PREPARATION EXAMPLES 4 TO 6

[0029] Irradiated UHMWPE molded articles were obtained by compression-deforming and cooling naturally similarly in Preparation Example 1 except that a dose of irradiation of γ-ray was changed to 10,000 J/kg (1,0 MR), 15,000 J/kg (1.5 MR) or 20,000 J/kg (2.0 MR) Each weight-average molecular weights of 10,000 J/kg (1.0 MR) irradiated article, 15,000 J/kg (1.5 MR) irradiated article and 20,000 J/kg (2.0 MR) irradiated article were infinite, and the melting points thereof were almost constant and were 138°C.

PREPARATION EXAMPLE 7

[0030] An irradiated UHMWPE molded article was obtained similarly in Preparation Example 1 except that after the irradiation of γ-ray (5,000 J/kg = 0,5 MR), the temperature was raised to 130°C and the compression-deformation to 1/3 was carried out under a pressure of 2.10^6 Pa (200 kgf/cm^2) for 5 minutes.

PREPARATION EXAMPLE 8

[0031] An irradiated UHMWPE molded article was obtained similarly in Preparation Example 1 except that after the compression molding, the isothermal crystallization was carried out for 10 hours at 120°C and then the natural cooling was carried out.

EXAMPLE 1

[0032] The test sample having a thickness of 7 mm and a diameter of 7 mm was prepared by cutting from the UHMWPE molded article obtained in each of Preparation Examples 1 to 8 and Comparative Preparation Examples 1 to 3, and a wear factor and coefficient of friction were evaluated by measuring a friction force and wear factor as the followings.

Testing apparatus and testing conditions:

[0033] The unidirectional Pin-On-Disc wear and friction testing machine manufactured by Research Center for Bio-medical Engineering, Kyoto University was used for the test.
[0034] The unidirectional-type testing machine is operated by pressing a test sample on a surface of a ceramic disc, which is rotating in the clockwise direction, by means of the arm-type loading method. The load can be varied by providing a weight to the one end of the arm. The rotation of the disc is transmitted to a bearing by way of a belt according to the rotation of an invertor-controlled motor. The testing speed was set to 50 mm/s. Also, all tests were carried out in 50 mℓ saline for 48 hours and the temperature of the liquid was kept at 25 ± 2°C.

Means to measure frictional force and wear volume:

[0035] A friction force was measured by a lever type dynamometer fixed to the arm portion of the testing machine. The friction force was recorded with a pen recorder with the lapse of time. The friction coefficients shown in test results (Table 1) were determined in case of a sliding distance of 8640 m (48 hours after tests begin).
[0036] The wear volume was evaluated by compressing the rotating disc of zirconia at a pressure of 1 MPa and by measuring the decreased thickness of the test sample with a non-contact type capacitance level gauge.
[0037] The test for each test sample was carried out three times under each loading condition, and the coefficient of friction and coefficient of abrasion were calculated in average value. In this case, the surface of the zirconia disc was made in intentionally roughened to Ra: 0.2 to 0.3, and the wear volume was measured after 48 hours.
[0038] Wear factor and coefficient of friction were calculated according to the equation of Dowson et al.

$$\text{Wear Factor (WF)} = \text{Wear volume (mm}^3\text{)}/\{\text{Load (N)} \times \text{Sliding distance (m)}\}$$

$$\text{Coefficient of friction (CF)} = \text{Friction force (N)}/\text{Load (N)}$$

[0039] The test results are shown in Table 1. With respect to the non-irradiated sample, there is no substantial difference in the wear factor (WF), that is, WF of 15.3×10^{-7} for the sample having the compression ratio at deformation (original thickness/thickness after compression-deformation) of 3, WF of 16.4×10^{-7} for the compression ratio of 4.5, and WF of 14.9×10^{-7} for the compression ratio of 6.
[0040] Remarkable decrease was observed, however, with respect to the 5000 J/kg (0.5 MR) irradiated sample, i.e. WF of 9.07×10^{-7} for the compression ratio of 3, WF of 2.78×10^{-7} for the compression ratio of 4.5, and WF of 5.31×10^{-8} for the compression ratio is 6.

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EXAMPLE 2

[0041] Characteristics of the UHMWPE molded articles obtained in Preparation Example 3 and Comparative Preparation Example 3 are shown in Table 2.

[0042] The heat of fusion and melting point were measured at a scan speed of 10°C /min by means of DSC-50 of SHIMADZU CORPORATION. And, the tensile strength and Young's modulus were measured at a tensile rate of 100 %/min by means of Autograph S-100 of SHIMADZU CORPORATION.

[0043] As shown in Table 2, the density and melting point of UHMWPE molded article obtained from the 0.5 MR irraidation test of Preparation Example 3 are higher and the tensile strength and Young's modulus thereof increase, as compared with those of the UHMWPE molded article obtained from the non-irradiation test of Comparative Preparation Example 3. Particularly, the melting point rises from 138.0° to 149.5°C.

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TABLE 1

$MR = 10^4 J/kg$

Preparation Example	Dose of irradiation MR	Compression deformation Temperature (°C)	Compression ratio	Cooling	Wear factor (WF)	Coefficient of friction (CF)
1	0.5	200	3	standing to cool	9.07×10^{-7}	0.11
2	0.5	200	4.5	standing to cool	2.78×10^{-7}	0.08
3	0.5	200	6	standing to cool	5.31×10^{-8}	0.03
4	1.0	200	3	standing to cool	7.35×10^{-7}	0.04
5	1.5	200	3	standing to cool	4.62×10^{-7}	0.02
6	2.0	200	3	standing to cool	8.31×10^{-8}	0.01
7	1.0	130	3	standing to cool	9.64×10^{-7}	0.12
8	1.0	200	3	allowed to cool after the isothermal crystallization for 10 hours at 120°C	2.53×10^{-8}	0.01
Comparative Preparation Example						
1	—	200	3	standing to cool	15.3×10^{-7}	0.14
2	—	200	4.5	standing to cool	16.4×10^{-7}	0.15
3	—	200	6	standing to cool	14.9×10^{-7}	0.12

TABLE 2

Sample	Density (g/cm^3)	Heat of fusion (cal/g)	Melting point (°C)	Tensile strength (kg/cm^2)	Young's modulus (kg/cm^2)
Comparative Preparation Example 3	0.931	31.6	138.0	0.3×10^3	1.36×10^4
Preparation Example 3	0.948	39.2	149.5	1.3×10^3	1.95×10^4

INDUSTRIAL APPLICABILITY

[0044] The ultra high molecular weight polyethylene molded article for artificial joints obtained according to the present invention has the molecular orientation or crystal orientation in the molded article, and is low in friction and is superior in abrasion resistance, and therefore is available as a component of artificial joints.
[0045] Further, the ultra high molecular weight polyethylene molded article for artificial joints of the present invention can be used as a component for artificial hip joints (artificial acetabular cup), a component for artificial knee joints (artificial tibial insert) and the socket for artificial elbow joints, and in addition to the medical use, it can be applied as materials for various industries by utilizing the characteristics such as low friction and superior abrasion resistance.

Claims

1. An ultra high molecular weight polyethylene molded block, **characterized by** having orientation of crystal plane, and obtainable by crosslinking an ultra high molecular weight polyethylene block, compression-deforming the crosslinked ultra high molecular weight polyethylene block, cooling and solidifying the deformed block in a compression-deformed state, said crystal plane being oriented in a direction parallel to the compression plane, and a density of said crosslinking being 0.1 to 10 crosslinking points per one molecular chain.

2. The molded blocks of claim 1, wherein a melting point of the ultra high molecular weight polyethylene block is 135°C to 155°C.

3. Artificial joints comprising the block of any one of claims 1 to 2.

4. A method for producing an ultra high molecular weight polyethylene molded block having orientation of crystal plane, **characterized in that** an ultra high molecular weight polyethylene block is crosslinked by irradiating a high energy ray to induce 0.1 to 10 crosslinking points per one molecular chain, the crosslinked ultra high molecular weight polyethylene block is compression-deformed after heating up to a compression deformable temperature and then cooled by a cooling method selected from water-cooling, air-cooling or standing to room temperature with keeping the deformed stae so that said crystal plane is oriented in a direction parallel to the compression plane.

5. The method of claim 4, wherein the high energy ray is a radioactive ray and a dose of the irradiation is 100 to 50,000 J/kg (0.01 to 5.0 MR).

6. The method of claim 4 or 5, wherein the compression-deformable temperature is a temperature in the range of a melting point of the crosslinked ultra high molecular weight polyethylene minus 50°C to the melting point plus 80°C.

7. The method of claim 4, 5 or 6 wherein a weight-average molecular weight of the ultra high molecular weight polyethylene before irradiation is 2 to 8 million.

8. The method of claim 4, 5, 6, or 7, wherein the cooling is carried out at a constant rate under 10 degree/minute.

Patentansprüche

1. Formblock aus Polyethylen mit ultrahohem Molekulargewicht, **dadurch gekennzeichnet, dass** er eine Orientierung der Kristallebene aufweist und erhältlich Ist durch Vernetzen eines Polyethylenblocks mit ultrahohem Molekulargewicht, Kompresslonsumformung des vernetzten Polyethylenblocks mit ultrahohem Molekulargewicht, Abkühlen und Verfestigen des umgeformten Blockes im Zustand der Kompressionsumformung, wobei die genannte Kristallebene in einer Richtung orientiert ist, die parallel zur Kompresslonsebene liegt, und die Dichte des genannten Vernetzens 0,1 bis 10 Vernetzungspunkte je eine Molekülkette beträgt.

2. Formblock nach Anspruch 1, worin der Schmelzpunkt des Blocks aus Polyethylen mit ultrahohem Molekulargewicht 135 bis 155°C beträgt.

3. Künstliche Gelenke, die den Block nach irgend einem der Ansprüche 1 bis 2 umfassen.

4. Verfahren zur Herstellung eines Formblocks aus Polyethylen mit ultrahohem Molekulargewicht, der eine Orientie-

rung der Kristallebene aufweist, **dadurch gekennzeichnet, dass** ein Block aus Polyethylen mit ultrahohem Molekulargewicht durch Bestrahlung mit Hochenerglestrahlung vernetzt wird, um 0,1 bis 10 Vernetzungspunkte pro Molekülkette zu Induzieren, der vernetzte Block aus Polyethylen mit ultrahohem Molekulargewicht nach Erwärmen auf die Kompressionsumformbarkeits-Temperatur kompressionsumgeformt wird und anschließend durch ein Kühlverfahren, das ausgewählt wird aus Wasserkühlung, Luftkühlung oder Stehenlassen bei Raumtemperatur unter Erhalt des umgeformten Zustands abgekühlt wird, so dass sich die genannte Kristallebene in einer Richtung orientiert, die parallel zur Kompressionsebene liegt.

5. Verfahren nach Anspruch 4, worin die Hochenerglestrahlung radioaktive Strahlung ist und die Dosierung der Strahlung 100 bis 50000 J/kg (0,01 bis 5,0 MR) beträgt.

6. Verfahren nach Anspruch 4 oder 5, worin die Kompresslonsumformbarkeits-Temperatur eine Temperatur ist, die Im Bereich des Schmelzpunktes des vernetzten Polyethylens mit ultrahohem Molekulargewicht minus 50°C bis zum Schmelzpunkt plus 80°C liegt.

7. Verfahren nach Anspruch 4, 5 oder 6, worin die massenmittlere Molekülmasse des Polyethylens mit ultrahohem Molekulargewicht vor der Bestrahlung 2 bis 8 Millionen beträgt.

8. Verfahren nach Anspruch 4, 5, 6 oder 7, worin das Abkühlen mit einer konstanten Geschwindigkeit von unterhalb 10 Grad/Minute durchgeführt wird.

Revendications

1. Bloc moulé de polyéthylène de poids moléculaire extrêmement élevé, **caractérisé en ce qu**'il présente une orientation de plan de cristal et pouvant être obtenu par réticulation d'un bloc de polyéthylène de poids moléculaire extrêmement élevé, par déformation par compression du bloc de polyéthylène de poids moléculaire extrêmement élevé, réticulé, par refroidissement et par solidification du bloc déformé dans un état déformé par compression, ledit plan de cristal étant orienté dans une direction parallèle au plan de compression et une densité de ladite réticulation étant de 0,1 à 10 points de réticulation pour une chaîne moléculaire.

2. Blocs moulés selon la revendication 1, dans lesquels un point de fusion du bloc de polyéthylène de poids moléculaire extrêmement élevé est de 135°C à 155°C.

3. Joints artificiels comprenant le bloc selon l'une quelconque des revendications 1 à 2.

4. Procédé pour la production d'un bloc moulé de polyéthylène de poids moléculaire extrêmement élevé ayant une orientation de plan de cristal, **caractérisé en ce qu**'un bloc de polyéthylène de poids moléculaire extrêmement élevé est réticulé par irradiation d'un rayon d'énergie élevée pour induire de 0,1 à 10 points de réticulation pour une chaîne moléculaire, le bloc de polyéthylène de poids moléculaire extrêmement élevé, réticulé est déformé par compression après chauffage jusqu'à une température de déformation par compression et est ensuite refroidi par un procédé de refroidissement choisi parmi un refroidissement à l'eau, un refroidissement à l'air ou un repos à température ambiante tout en maintenant l'état déformé de telle sorte que ledit plan de cristal est orienté dans une direction parallèle au plan de compression.

5. Procédé selon la revendication 4, dans lequel le rayon d'énergie élevée est un rayon radioactif et une dose de l'irradiation est de 100 à 50 000 J/kg (0,01 à 5,0 MR).

6. Procédé selon la revendication 4 ou 5, dans lequel la température de déformation par compression est une température dans l'intervalle d'un point de fusion du polyéthylène de poids moléculaire extrêmement élevé, réticulé moins 50°C au point de fusion plus 80°C

7. Procédé selon la revendication 4, 5 ou 6, dans lequel un poids moléculaire moyen en poids du polyéthylène de poids moléculaire extrêmement élevé avant l'irradiation est de 2 à 8 millions.

8. Procédé selon la revendication 4, 5, 6 ou 7, dans lequel le refroidissement est réalisé à une vitesse constante inférieure à 10 degré/min.